



Variations and sources of nitrous acid (HONO) during a severe pollution episode in Beijing in winter 2016

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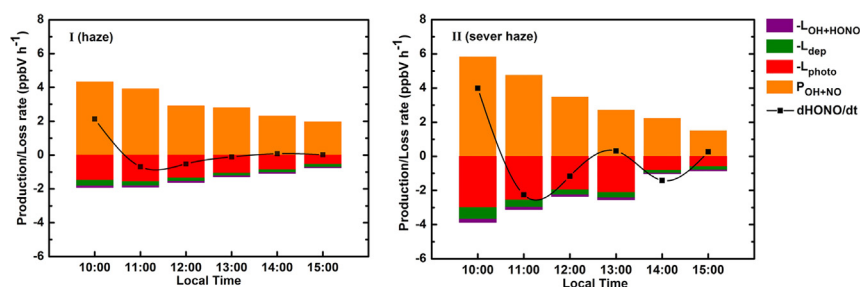
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HIGHLIGHTS

- High HONO concentrations were observed in a severe pollution episode in Beijing.
- The NO₂ conversion was not an important pathway to form HONO at nighttime.
- Direct emissions could be critical to the observed HONO.
- The homogeneous reaction could be a noticeable HONO source.
- Good relation of HONO with PM_{2.5} implied a chemical link between HONO and PM_{2.5}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 June 2018

Received in revised form 6 August 2018

Accepted 10 August 2018

Available online 11 August 2018

Editor: Jianmin Chen

Keywords:

Nitrous acid measurement

Haze

Vehicle emissions

Homogeneous reaction

Daytime HONO budget

ABSTRACT

HONO is an important precursor of OH radical and plays a key role in atmospheric chemistry, but its source and formation mechanism remain uncertain, especially during complex atmospheric pollution processes. In this study, HONO mixing ratios were measured by a custom-made instrument during a severe pollution event from 16 to 23 December 2016, at an urban area of Beijing. The measurement was divided into three periods: I (haze), II (severe haze) and III (clean), according to the levels of PM_{2.5}. This pollution episode was characterized by high levels of NO (75 ± 39 and 94 ± 40 ppbV during periods I and II, respectively) and HONO (up to 10.7 ppbV). During the nighttime, the average heterogeneous conversion frequency during the two haze periods were estimated to be 0.0058 and 0.0146 h⁻¹, and it was not the important way to form HONO. Vehicle emissions contributed 52% ($\pm 16\%$) and 40% ($\pm 18\%$) to ambient HONO at nighttime during periods I and II. The contribution of homogeneous reaction of NO with OH should be reconsidered under high-NO_x conditions and could be noticeable to HONO sources during this pollution event. Furthermore, HONO was positively correlated with PM_{2.5} during periods I and II, suggesting a potential chemical link between HONO and haze particles.

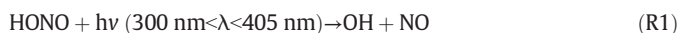
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1. Introduction

Hydroxyl (OH) radical is a major oxidant in the troposphere and plays an important role in the ability of the atmosphere to “cleanse itself” (Heard and Pilling, 2003). In addition, OH radical affects many chemical and photochemical processes and contributes to the formation of O₃ and PANs (peroxyacyl nitrates) (Heard and Pilling, 2003; Hofzumahaus et al., 2009). As an important precursor of OH radical, HONO is a significant species in the tropospheric photochemistry (Alicke et al., 2002; Kleffmann et al., 2005; Lammel and Cape, 1996). Recent studies proposed that HONO photolysis (R1) produced 34%–56% of OH radical in the whole daytime (Alicke et al., 2002; Hendrick et al., 2014; Kleffmann, 2007; Michoud et al., 2012) and produced about 80% of OH radical in the early morning (Acker et al., 2006). Moreover, in pollution episodes, OH radical is almost generated by HONO photolysis (Aumont et al., 2003; Platt and Perner, 1980).



In recent years, HONO has been extensively discussed owing to its ability of initiating and accelerating daytime photochemistry. HONO sources were generally grouped into direct emissions, homogeneous reactions, heterogeneous reactions, surface-absorbed nitric acid and/or particulate nitrate photolysis and soil nitrite emissions (Spataro and Ianniello, 2014, and references therein). Although vehicle emissions contribute to ambient HONO, the relative contribution is controversial, as there are different types of vehicles and various vehicle emission standards (Trinh et al., 2017). The reaction of NO with OH (R2) is widely accepted as a key homogeneous pathway to form HONO, especially when NO and OH are high during the daytime in polluted areas (e.g. Li et al., 2012). Due to the low level of OH radical, this homogeneous reaction was reported to be insignificant during the nighttime (Wong et al., 2011). However, recent studies found that nocturnal OH radical were relatively high in China, for example, OH radical was mostly above $3 \times 10^5 \text{ cm}^{-3}$ in Wangdu in summer 2014. Therefore, homogeneous formation could play an important role in HONO formation (Tan et al., 2017; Tong et al., 2015). Laboratory studies suggested that heterogeneous conversion of NO₂ into HONO is an important HONO source (Ammann et al., 1998; Broske et al., 2003; Finlayson-Pitts et al., 2003; George et al., 2005; Kleffmann et al., 1999; Stemmler et al., 2007), but the exact mechanisms are unclear. Although substantial field and laboratory studies were carried out to investigate formation mechanisms of HONO in the troposphere, HONO sources and their relative contributions to ambient HONO are still unclear, especially under pollution conditions.



Beijing, a rapidly developing megacity in China, has been suffering from haze pollution for several years. For example, only during January 2013, the PM_{2.5} level in the urban area of Beijing exceeded the Second Grade National Standard of China ($75 \mu\text{g m}^{-3}$) for 22 days, meaning that people were exposed to polluted air for nearly the whole month (He et al., 2014). Although the government rapidly took the strict control measures for anthropogenic emissions, such as vehicle control and production restriction measures, substantial amounts of haze events have occurred since 2013. Haze is usually caused by secondary aerosol particles (Guo et al., 2014; Huang et al., 2014; Liu et al., 2017a). Several studies indicated that high level of HONO produced high level of OH radical, resulting in increased secondary aerosols (An et al., 2013; Huang et al., 2014). Therefore, the source and formation mechanism of HONO are crucial for better understanding the atmospheric chemistry during pollution episodes. Numerous field observations were performed to investigate mixing ratios and potential sources of HONO in Beijing (shown in Table 1), but the studies for the level and formation mechanism of HONO during haze episodes are still limited.

Beijing has suffered from a severe haze pollution from 16 to 21 December, in winter 2016. The government issued the first red alert for heavy air pollution in 2016, and rapidly took the most strict control measures for anthropogenic emissions, such as vehicle control and production restriction measures. Hereby, we performed a field measurement of HONO at an urban area of Beijing during 16 to 23 December 2016, including this severe pollution process. Simultaneous trace gases (SO₂, CO, NO, NO₂ and O₃), PM_{2.5}, and meteorological parameters were also obtained in this measurement. The objectives of this study are to explore levels and variations of HONO and to evaluate relative contributions of different HONO sources during this pollution event in Beijing.

2. Experimental

2.1. Measurement site

The atmospheric HONO mixing ratios and meteorological parameters were measured on the third floor of No.2 building (~10 m above the ground level) at Institute of Chemistry, Chinese Academy of Sciences (ICCAS, 39°59′22.68″N, 116°19′21.58″E) in Beijing. About 480 m to the south is the Fourth Ring Road. It is a typical urban site and was described in details in previous works (Hou et al., 2016; Tong et al., 2016; Tong et al., 2015). The observation was performed from 16 to 23 December 2016, including a pollution period and a following clean period. In addition, mixing ratios of trace gases (including SO₂, CO, NO, NO₂ and O₃) and PM_{2.5} were simultaneously acquired from Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (RCEES, 40°00′28″N, 116°20′15″E), 2.8 km northeast from the ICCAS site, which is also adjacent to the Fourth Ring Road and has similar conditions with few spatial differences of NO₂ and NO_x levels from the ICCAS site. Black carbon was measured at the Tower Branch of the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP, 39°58′54.9078″N, 116°23′4.7904″E), about 5 km southeast from the ICCAS site. The IAP site is between the North Third and Fourth Ring Roads, which is surrounded by condensed population and heavy traffic, and thus it is a typical urban area of Beijing, similar to two sites above.

2.2. Measurement instruments

The atmospheric HONO mixing ratios were conducted using a custom-made HONO analyzer which was described in details elsewhere (Hou et al., 2016; Tong et al., 2016; Tong et al., 2015). Briefly, the principle of HONO analyzer is similar to long path absorption photometer (LOPAP) (Heland et al., 2001; Kleffmann et al., 2002). HONO is fast collected by a two-channel glass stripping coil with an absorption solution (0.06 M sulfanilamide in 1 M HCl) to form a stable diazonium salt which then reacts with a dye solution [0.8 mM N-(1-naphthyl) ethylenediamine-dihydrochloride]. Then an azo dye is formed and finally pumped into a 50 cm liquid waveguide capillary cell (LWCC). A subsequent detection is performed by an optical absorption spectrometer (Ocean Optics, SD2000). The final HONO concentration is the difference of signals between the two channels. The liquid flow rate is 0.3 mL min⁻¹ with a sampling gas flow rate of 1.0 L min⁻¹. The detection limit of the instrument is 200 pptV with a response time of 15 min. A side by side intercomparison between the custom-made HONO analyzer and a commercial LOPAP instrument was carried out in our previous study, which certified the accuracy and reliability of HONO analyzer (Hou et al., 2016).

The meteorological parameters consisting of air temperature (T), relative humidity (RH), wind speed (WS) and wind direction (WD) were measured by a vaisala weather transmitter (WXT520). The mixing ratios of SO₂, CO, NO, NO₂, NO_x and O₃ were determined using SO₂ analyzer (Thermo Scientific, Model 43i), CO analyzer (Thermo Scientific, Model 48i), NO_x analyzer (Thermo Scientific, Model 42i) and O₃ analyzer (Thermo Scientific, Model 49i) with detection limits of 1 ppbV,

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