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Original article

Impact of environmental variables on the reduction of nitric acid by proxies for volatile organic compounds emitted by motor vehicles

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ABSTRACT

Recent work has identified nitric acid (HNO₃) as a potential precursor of nitrous acid (HONO), which is an important source of oxidants that regulate ozone and particulate pollution. Recent work in our laboratory has indicated that the reduction of HNO₃ to HONO can occur homogeneously in the presence of surrogates for volatile organic compounds (VOCs) emitted by motor vehicles. This study focuses on the impact of environmental variables on the rate of formation of HONO in this process. The observed base case (25.0 °C and ~20.0% relative humidity (RH)) HONO formation rate was 0.54 ± 0.09 ppb h⁻¹, values comparable to enhancements observed in HONO during morning rush hour in Houston, TX. The rate was enhanced at lower temperatures of ~20.0 °C, but the rate remained statistically similar (1σ) for experiments conducted at temperatures of 25 °C, 30 °C, and 35 °C. The assumption that multiple reactive components of the VOC mixture react with HNO₃ is supported by this observation, and the relative importance of each reactive species in the reaction may vary with temperature. The enhanced rate at lower temperatures could make the proposed reaction mechanism more important at night. The formation rate of HONO does not change substantially when initial HNO₃ concentration is varied between 400 and 4600 ppt, suggesting that the concentration of reactive VOCs was the limiting factor. The reduction of HNO₃ to HONO appears not to occur heterogeneously on the aerosol surfaces tested. The presence of ~120 ppb of ammonia has no observable impact on the reaction. However, it is likely that UV irradiation (λ = 350 nm) decreases the formation rate of HONO either by consuming the reactive VOCs involved or by directly interfering with the reaction. The “renoxification” of less reactive HNO₃ to more reactive HONO has significant implications for daytime ozone and particulate pollution.

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1. Introduction

Nitrous acid (HONO) is an important trace gas in the regional and global troposphere. It can have significant air quality

implications due to its photolysis, yielding nitrogen oxide (NO) and the hydroxyl radical (OH) (Atkinson, 2000):



The OH radical serves as a strong oxidant in the atmosphere and is partly responsible for the chemical processes that lead to the formation of tropospheric ozone (O₃) (Finlayson-Pitts and Pitts, 1997) and secondary particulate matter (PM) (Kanakidou et al., 2005). With nitrogen dioxide (NO₂), NO contributes to total nitrogen oxide (NO_x) levels. The potential of a regional air mass to

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produce O₃ depends strongly on the relative abundance of volatile organic compounds (VOCs) and NO_x. Because HONO influences NO_x levels, O₃ pollution levels are highly sensitive to HONO levels under particular conditions (Harris et al., 1982; Lei et al., 2004; Carter and Seinfeld, 2012). Harris et al. (1982) observed increases in O₃ dosages up to a factor of 3 when 10 ppb of HONO is included in model simulations. Using a three-dimensional chemical transport model, Lei et al. (2004) estimated up to 12 ppb enhancements in O₃ levels in Houston, TX, due to a proposed heterogeneous source of HONO. Zero-dimensional model simulations of O₃ formation episodes in the Upper Green River Basin in Wyoming during winter predicted strong O₃ sensitivity to HONO levels (Carter and Seinfeld, 2012).

Nitrous acid mixing ratios observed at various urban sites range from 0.4 to 8.0 ppb at night and 100–300 ppt during the day (Harris et al., 1982; Harrison et al., 1996; Kleffmann, 2007; Wong et al., 2011; Indarto, 2012), while concentrations at rural sites were 10–200 ppt (Cape et al., 1992; Zhou et al., 2002, 2011). A known source of HONO during daytime in polluted environments is the reaction between OH and NO (Atkinson, 2000):



Nitrous acid builds up overnight from (R2) (when OH and NO persist without sunlight) and other sources and photolyzes in the morning, causing a spike in OH and NO_x, resulting in accelerated O₃ production (Harris et al., 1982). Nitrous acid sources other than (R2) are thus highly important due to their potential to contribute to both daytime and nighttime HONO levels. Modeling studies have concluded that HONO sources are still missing from current hydrogen oxide (HO_x) and NO_x chemistry models, resulting in the underprediction of HONO or O₃ levels (Grannas et al., 2007; Wong et al., 2011; Carter and Seinfeld, 2012).

A number of recent studies have documented possible sources of HONO from HNO₃ or NO₂. Kleffmann (2007) proposed several formation mechanisms: heterogeneously on surfaces treated with HNO₃, from the reduction of NO₂ on photosensitized organic surfaces, and via photolysis of ortho-substituted nitroaromatics. Similarly, photolytic conversion of NO₂ to HONO on polycyclic aromatic hydrocarbon films was observed by Cazoir et al. (2014). Grannas et al. (2007) summarized several HONO formation mechanisms in a snowpack. In urban New Zealand, Reisinger (2000) observed a good correlation between HONO/NO₂ (a metric for the relative abundance of HONO) and aerosol surface density, indicating a heterogeneous HONO source. Nitrous acid forms on the surface of soot particles from NO₂, but the reaction is not considered a major contributor to HONO under typical ambient conditions (Ammann et al., 1998; Kalberer et al., 1999). Kirchstetter et al. (1996) measured vehicular emissions of HONO in the Caldecott Tunnel, but the observed HONO/NO₂ ratios were much lower than the nighttime values measured under ambient conditions. In addition, recent airborne measurements coupled with zero-dimensional model simulations inferred a strong gas-phase source within the residual layer with formation rates that scaled with HONO photolysis rates (Li et al., 2014). The authors argued that this unknown source could dominate overall HONO production in the planetary boundary layer, exceeding surface HONO sources. The proposed ultraviolet (UV)-dependent HONO source was likely internal (from the reaction of NO_x and/or HO_x). Liu et al. (2014) proposed a substantial heterogeneous HONO source from the hydrolytic disproportionation of NO₂ on aerosol to help explain missing daytime HONO sources in China. Flow tube studies by VandenBoer et al. (2015) suggested a nighttime soil sink of HONO, leading to daytime acid displacement and release of HONO. A review of the current state of the science for HONO can be found in Spataro and Ianniello (2014).

In September 2006 in Houston, TX, Ziemba et al. (2010) observed HNO₃ depletion concurrent with increases in HONO concentrations and aerosol surface area dominated by a proxy for primary organic aerosol (POA). The authors hypothesized a heterogeneous reaction between HNO₃ and POA to form HONO, which supports the findings from previous studies that document the heterogeneous reduction of HNO₃ (Zhou et al., 2002; Rivera-Figueroa et al., 2003; Zhou et al., 2003, 2011).

In an effort to better understand the phenomenon observed by Ziemba et al. (2010), Rutter et al. (2014) performed a series of flow tube experiments in which gaseous HNO₃ was observed to be reduced homogeneously to HONO by VOCs representative of those emitted from motor vehicles via the hypothesized reaction:



The reported formation rate of HONO was 0.3 ± 0.1 ppb h⁻¹ under a defined base case of 25.0 °C and RH of ~20%. The HONO formation rates decreased with increasing RH. Increased surface area in the flow-tube (Teflon® Raschig rings and/or a surrogate for vehicular POA) had no impact on HONO formation. The experiments described here used a slightly modified and improved version of the flow-tube system of Rutter et al. (2014) to further characterize this HONO formation reaction by varying temperatures and HNO₃ concentrations, irradiating, or adding ammonia (NH₃) or mineral dust surrogates. These experiments are designed to improve our understanding of the importance of the proposed HONO formation reaction under varying ambient conditions and to assess its potential to enhance HONO levels in the atmosphere.

2. Experimental

2.1. General information

The flow-tube system used in this study is described by Rutter et al. (2014), with improvements and additional instrumentation described below. Briefly, HNO₃ gas and VOCs from a specific blend of vehicle engine oil (Supporting material, Table S1) were introduced into a quartz flow reactor, which is located in a temperature-controlled chamber. Nitric acid was generated from a permeation device (Dynacal, VICI Metronics, Poughkeepsie, NY), and engine oil particles along with VOCs were introduced using a TSI 3076 atomizer (Shoreview, MN) with a Teflon® filter in-line when the particles were not desired. A combustion VOC surrogate was not used for this study as the original intent was to use reduced organics from motor oil (Rutter et al., 2014); this avoids possible HONO artifacts from combustion exhaust (Kirchstetter et al., 1996). A recent tunnel study showed that a large portion of vehicular POA is similar in composition to unburned motor oil (Worton et al., 2014). The VOCs used in this study were intended to serve as surrogates for VOCs produced from the volatilization of vehicular POA under ambient conditions. The outflow from the flow-tube was sampled by a refurbished on-line mist chamber-ion chromatograph (MC/IC) system (Rutter et al., 2014) to obtain 10-min HONO and HNO₃ concentrations. This measurement technique has been tested and characterized extensively (Talbot et al., 1990; Dibb et al., 1994, 1998, 2002) and showed good comparison with Differential Optical Absorption Spectroscopy (Stutz et al., 2010). A new quartz flow-tube with dimensions identical to those of the reactor in Rutter et al. (2014) was used and was passivated by a non-reactive halocarbon wax coating to minimize wall reactions. Instrumentation used to measure temperature, RH, and particle number concentration were outlined in Rutter et al. (2014). The instrumentation for measuring NH₃ is described below.

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