

3-1-2016

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Recommended Citation

Leong, Y. J., A. P. Rutter, H. Y. Wong, C. V. Gutierrez, M. Junaid, E. Scheuer, L. Gong, R. Lewicki, J. E. Dibb, F. K. Tittel, and R. J. Griffin (2016), Impact of environmental variables on the reduction of nitric acid by proxies for volatile organic compounds emitted by motor vehicles, *Atmospheric Pollution Research*, 7, 221-227, <https://dx.doi.org/10.1016/j.apr.2015.09.006>

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1 **Impact of Environmental Variables on the Reduction of Nitric Acid by Proxies for Volatile Organic**
2 **Compounds Emitted by Motor Vehicles**

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20 **Abstract**

21 Recent work has identified nitric acid (HNO₃) as a potential precursor of nitrous acid (HONO),
22 which is an important source of oxidants that regulate ozone and particulate pollution. Recent
23 work in our laboratory has indicated that the reduction of HNO₃ to HONO can occur
24 homogeneously in the presence of surrogates for volatile organic compounds (VOCs) emitted by
25 motor vehicles. This study focuses on the impact of environmental variables on the rate of
26 formation of HONO in this process. The observed base case (25.0°C and ~20.0% relative humidity
27 (RH)) HONO formation rate was 0.54 ± 0.09 ppb hr⁻¹, values comparable to enhancements
28 observed in HONO during morning rush hour in Houston, TX. The rate was enhanced at lower
29 temperatures of ~20.0°C, but the rate remained statistically similar (1σ) for experiments
30 conducted at temperatures of 25°C, 30°C, and 35°C. The assumption that multiple reactive
31 components of the VOC mixture react with HNO₃ is supported by this observation, and the relative
32 importance of each reactive species in the reaction may vary with temperature. The enhanced

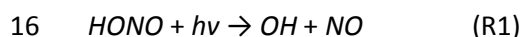
1 rate at lower temperatures could make the proposed reaction mechanism more important at
2 night. The formation rate of HONO does not change substantially when initial HNO₃ concentration
3 is varied between 400 and 4 600 ppt, suggesting that the concentration of reactive VOCs was the
4 limiting factor. The reduction of HNO₃ to HONO appears not to occur heterogeneously on the
5 aerosol surfaces tested. The presence of ~120 ppb of ammonia has no observable impact on the
6 reaction. However, it is likely that UV irradiation ($\lambda = 350$ nm) decreases the formation rate of
7 HONO either by consuming the reactive VOCs involved or by directly interfering with the reaction.
8 The “renoxification” of less reactive HNO₃ to more reactive HONO has significant implications for
9 daytime ozone and particulate pollution.

10 **Keywords**

11 Nitrous acid; nitric acid; volatile organic compounds; flow tube; reduction-oxidation

12 **1. Introduction**

13 Nitrous acid (HONO) is an important trace gas in the regional and global troposphere. It can have
14 significant air quality implications due to its photolysis, yielding nitrogen oxide (NO) and the
15 hydroxyl radical (OH) (Atkinson, 2000):



17 The OH radical serves as a strong oxidant in the atmosphere and is partly responsible for the
18 chemical processes that lead to the formation of tropospheric ozone (O₃) (Finlayson-Pitts and Pitts,
19 1997) and secondary particulate matter (PM) (Kanakidou et al., 2005). With nitrogen dioxide (NO₂),
20 NO contributes to total nitrogen oxide (NO_x) levels. The potential of a regional air mass to produce
21 O₃ depends strongly on the relative abundance of volatile organic compounds (VOCs) and NO_x.
22 Because HONO influences NO_x levels, O₃ pollution levels are highly sensitive to HONO levels under
23 particular conditions (Harris et al., 1982; Lei et al., 2004; Carter and Seinfeld, 2012). Harris et al.
24 (1982) observed increases in O₃ dosages up to a factor of 3 when 10 ppb of HONO is included in
25 model simulations. Using a three-dimensional chemical transport model, Lei et al. (2004)
26 estimated up to 12 ppb enhancements in O₃ levels in Houston, TX, due to a proposed
27 heterogeneous source of HONO. Zero-dimensional model simulations of O₃ formation episodes in
28 the Upper Green River Basin in Wyoming during winter predicted strong O₃ sensitivity to HONO
29 levels (Carter and Seinfeld, 2012).

30 Nitrous acid mixing ratios observed at various urban sites range from 0.4 to 8.0 ppb at night and
31 100 to 300 ppt during the day (Harris et al., 1982; Harrison et al., 1996; Kleffmann, 2007; Wong et
32 al., 2011; Indarto, 2012), while concentrations at rural sites were 10 to 200 ppt (Cape et al., 1992;
33 Zhou et al., 2002; Zhou et al., 2011). A known source of HONO during daytime in polluted
34 environments is the reaction between OH and NO (Atkinson, 2000):



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

8 A number of recent studies have documented possible sources of HONO from HNO₃ or NO₂.
9 Kleffmann (2007) proposed several formation mechanisms: heterogeneously on surfaces treated
10 with HNO₃, from the reduction of NO₂ on photosensitized organic surfaces, and via photolysis of
11 ortho-substituted nitroaromatics. Similarly, photolytic conversion of NO₂ to HONO on polycyclic
12 aromatic hydrocarbon films was observed by Cazoir et al. (2014). Grannas et al. (2007)
13 summarized several HONO formation mechanisms in a snowpack. In urban New Zealand, Reisinger
14 (2000) observed a good correlation between HONO/NO₂ (a metric for the relative abundance of
15 HONO) and aerosol surface density, indicating a heterogeneous HONO source. Nitrous acid forms
16 on the surface of soot particles from NO₂, but the reaction is not considered a major contributor to
17 HONO under typical ambient conditions (Ammann et al., 1998; Kalberer et al., 1999). Kirchstetter
18 et al. (1996) measured vehicular emissions of HONO in the Caldecott Tunnel, but the observed
19 HONO/NO₂ ratios were much lower than the nighttime values measured under ambient conditions.
20 In addition, recent airborne measurements coupled with zero-dimensional model simulations
21 inferred a strong gas-phase source within the residual layer with formation rates that scaled with
22 HONO photolysis rates (Li et al., 2014). The authors argued that this unknown source could
23 dominate overall HONO production in the planetary boundary layer, exceeding surface HONO
24 sources. The proposed ultraviolet (UV)-dependent HONO source was likely internal (from the
25 reaction of NO_x and/or HO_x). Liu et al. (2014) proposed a substantial heterogeneous HONO source
26 from the hydrolytic disproportionation of NO₂ on aerosol to help explain missing daytime HONO
27 sources in China. Flow tube studies by VandenBoer et al. (2015) suggested a nighttime soil sink of
28 HONO, leading to daytime acid displacement and release of HONO. A review of the current state
29 of the science for HONO can be found in Spataro and Ianniello (2014).

30 In September 2006 in Houston, TX, Ziemba et al. (2010) observed HNO₃ depletion concurrent with
31 increases in HONO concentrations and aerosol surface area dominated by a proxy for primary
32 organic aerosol (POA). The authors hypothesized a heterogeneous reaction between HNO₃ and
33 POA to form HONO, which supports the findings from previous studies that document the
34 heterogeneous reduction of HNO₃ (Zhou et al., 2002; Rivera-Figueroa et al., 2003; Zhou et al.,
35 2003; Zhou et al., 2011).

36 In an effort to better understand the phenomenon observed by Ziemba et al. (2010), Rutter et al.
37 (2014) performed a series of flow tube experiments in which gaseous HNO₃ was observed to be
38 reduced homogeneously to HONO by VOCs representative of those emitted from motor vehicles
39 via the hypothesized reaction:



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

10 **2. Experimental**

11 **2.1 General Information**

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

33 In this study, the base case experiments were conducted at a temperature of 25°C and a RH of
34 ~20% while maintaining a mean HNO₃ concentration of 2.4 ppb and a constant level of VOCs in the
35 flow-tube reactor. For each experiment, the flow-tube reactor was allowed to equilibrate at the
36 desired conditions (concentrations of HNO₃ and VOCs, temperature, RH, and other variables). The
37 formation rates of HONO (f_{HONO} , ppb hr⁻¹) were calculated using the step change in HONO
38 concentrations when VOCs were removed:

$$39 \quad f_{\text{HONO}} = ([\text{HONO}]_t - [\text{HONO}]_0) / t_{\text{res}} \quad \text{Equation (1)}$$

1 where $[HONO]_t$ (in ppb) was the average steady-state HONO concentration measured when VOCs
2 were present to react with HNO_3 , $[HONO]_0$ was measured after VOCs were removed and only
3 HNO_3 was present, and t_{res} is the average residence time of all gases in the flow-tube (150 s).
4 Detailed descriptions of a typical experiment can be found in Rutter et al. (2014), and all
5 experiments described in this study follow the same procedures except the modifications
6 mentioned below. Additional experimental information is provided in the Supporting Material and
7 Table S2.

8 Engine oil particles (100 nm, $< 150 \text{ \#/cm}^3$) were shown in Rutter et al. (2014) to have no effect on
9 the reaction. During several tests, larger concentrations of motor oil particles were injected (up to
10 1400 \#/cm^3) into the mixture of VOCs and HNO_3 , and the particles had no observable impact on
11 HONO levels. Therefore, for all experiments presented here motor oil particles were not
12 considered relevant and were excluded by filtering the output from the atomizer upstream of the
13 flow tube reactor. Figure 1 depicts the experimental setup used in this study. A detailed diagram
14 for the delivery of HNO_3 and VOCs can be found in Rutter et al. (2014).

15 Variations to the base case experiments were achieved by independently varying chamber
16 temperature or HNO_3 concentration or by introducing UV irradiation, NH_3 , or mineral dust aerosol
17 surrogate to the system. When a parameter was altered or a new constituent was added, all other
18 base case variables remained unchanged. Apart from HNO_3 and NH_3 experiments discussed in
19 sections 2.3 and 2.4, all experiments in this study were conducted at initial HNO_3 concentrations of
20 $\sim 2\text{-}4$ ppb for consistency with the experiments of Rutter et al. (2014) and the field measurements
21 of Ziemba et al. (2010).

22 **2.2 Temperature**

23 This study aims to investigate the sensitivity of f_{HONO} to reaction temperature. Because the
24 proposed reduction reaction of HNO_3 by VOCs may involve simultaneous reactions of different
25 reactive VOCs of the engine oil blend, the temperature dependence of the overall formation rate
26 is not expected to follow Arrhenius behavior. Investigation of temperature dependence is
27 achieved by a temperature-controlled environmental test chamber (Espec North America Inc.,
28 Hudsonville, MI). The flow-tube and other components were allowed to equilibrate at the desired
29 set-point temperature before an experiment. The measured reactor outflow temperatures were
30 within $\sim 1^\circ\text{C}$ of the set-point chamber temperatures. The temperature range tested here is relevant
31 for the conditions observed in the 2006 Houston field study.

32 **2.3 HNO_3 Concentration**

33 Initial HNO_3 mixing ratios were kept relatively constant in the experiments by Rutter et al. (2014),
34 but minor fluctuations in HNO_3 between experiments were impossible to avoid. Nitric acid
35 concentration was not considered important by Rutter et al. (2014) because the HNO_3 levels were
36 in excess of the estimated 200 - 300 ppt reactive VOCs in the reactor. Here, experiments
37 conducted at different initial concentrations of HNO_3 were used to probe this hypothesis and to
38 investigate potential impacts of HNO_3 levels on the proposed reaction.

1 The steady-state HNO₃ concentrations in the flow-tube were varied in these experiments by
2 operating the permeation device at different temperatures or by shutting off its supply entirely.
3 Holding other parameters constant, HNO₃ mixing ratios of approximately 4.0 ppb, 1.5 ppb, and 0.4
4 ppb were achieved. The corresponding experiments are henceforth referred to as high HNO₃,
5 medium HNO₃, and low HNO₃ experiments.

6 **2.4 NH₃**

7 Ammonia reacts with HNO₃ to form ammonium nitrate (NH₄NO₃), which transitions to the
8 particulate phase when specific thermodynamic criteria are met. This reaction is hypothesized as a
9 potential competing reaction and was studied in the flow-tube reactor by the addition of NH₃.
10 Experiments were performed by injecting 118.0 ± 2.0 ppb of gas-phase NH₃ to the flow-tube
11 reactor. A 1-ppm NH₃ cylinder supplied the NH₃ gas stream, which was diluted upon entering the
12 reactor. Ammonia concentrations were monitored using a 10.4-μm external cavity quantum
13 cascade laser that has been well characterized and tested (Gong et al., 2011; Gong et al., 2013).
14 The instrument has a detection limit of 0.7 ppb and an accuracy of 7%, with a maximum time-
15 resolution of 1 s. Because the MC collection efficiencies for HNO₃ and HONO already exceed 95%
16 (Dibb et al., 1994), NH₃ is not expected to cause interferences in HNO₃ and HONO measurements.
17 There was no evidence of artifacts from particulate NH₄NO₃ because the MC/IC sample stream
18 was filtered.

19 **2.5 UV Irradiation**

20 A HONO artifact at a forested field site correlated with UV intensity, possibly due to the
21 photochemical conversion of HNO₃ to HONO on the wall of a glass sampling manifold (Zhou et al.,
22 2002). Laboratory experiments conducted by Zhou et al. (2003) found evidence that photolysis of
23 adsorbed HNO₃ on Pyrex surfaces yields HONO, and Zhou et al. (2011) found a significant HONO
24 daytime source from the photolysis of HNO₃ on forest canopies. These findings emphasize the
25 potential role of UV irradiation in the conversion of HNO₃ to HONO. Despite the observations of
26 Rutter et al. (2014) and Ziemba et al. (2010) that light is not required for the proposed (R3) to
27 proceed, it is hypothesized that UV irradiation may either accelerate (R3) or dampen it by
28 consuming the reactive VOCs involved. Thus, experiments were conducted to test the sensitivity of
29 f_{HONO} to UV irradiation.

30 Four 4-ft, 40W Sylvania 350BL lights (Osram Sylvania, Danvers, MA) irradiated the flow-tube
31 reactor for one set of experiments. Totalling 160W of output, these tubes were mounted above the
32 reactor and were distributed evenly along the length of the reactor. The reactor and lights were
33 encased in Mylar reflective material to maximize light intensity and to ensure uniform distribution
34 of the artificial light (peak $\lambda = 350$ nm). The same type of lights was used in the chamber
35 experiments of Cocker et al. (2001). This wavelength produces maximum NO₂ photolysis rates
36 (Carter et al., 1995) and falls within the UV-A spectrum (320 to 400 nm), which has been reported
37 to photolyze species such HONO (Stutz et al., 2000; Alicke et al., 2002). Thus, the lamps were
38 considered a viable starting point to test for direct interferences on the hypothesized HONO
39 formation reaction.

1 2.6 Mineral Dust Aerosol Surfaces

2 Field data collected in Houston during 2006 showed the potential for heterogeneous reduction of
3 HNO_3 into HONO on urban aerosol (Ziemba et al., 2010). However, Rutter et al. (2014) showed
4 that the HONO formation reaction does not occur heterogeneously on engine oil particles or on a
5 large surface area of Teflon® material. Grassian (2002) observed HNO_3 heterogeneous uptake on
6 mineral dust (alumina (Al_2O_3) and silica (SiO_2)) surfaces and heterogeneous HONO production
7 reactions from NO_2 on soot or SiO_2 particles. Gustafsson et al. (2008) observed heterogeneous
8 production of HONO on mineral dust (from the Gobi desert) from NO_2 and water. Because mineral
9 dust aerosols have more polar surfaces when compared to the engine oil and Teflon® surfaces,
10 they are hypothesized to be better candidates for heterogeneous conversion of HNO_3 to HONO.
11 Two types of atmospherically abundant mineral dust materials were chosen for these
12 experiments: carboxylate-doped SiO_2 and Al_2O_3 .

13 Aqueous dispersions of size-calibrated 100-nm monodisperse spherical particles composed of
14 either carboxylated- SiO_2 or pure Al_2O_3 (Corpuscular Inc., Cold Spring, NY) were used to generate
15 aerosols for these experiments. These solutions were nebulized using an atomizer and
16 subsequently dried using a diffusion-dryer and a heater ($87.5 \pm 1.5^\circ\text{C}$).

17 3. Results and Discussion

18 3.1 Base Case Results

19 Compared with the previous flow-tube study, the average base case f_{HONO} of 0.54 ± 0.09 ppb hr^{-1}
20 (Table 1) agrees better with the observed 2006 Houston value of 0.6 ± 0.3 ppb hr^{-1} (Ziemba et al.,
21 2010; Rutter et al., 2014). This could be attributed to improved measurement accuracy due to the
22 refurbished MC/IC system. This observation also suggests that the reduction of HNO_3 to HONO by
23 the reactive components of vehicular VOCs that were co-emitted with POA (Rutter et al., 2014)
24 could be a dominant contributor to HONO formation events observed in Houston. The comparison
25 here is qualitative because meteorology and vertical mixing conditions are highly variable in the
26 atmosphere, and temperature ranged from 20.0 to 35.0°C during this field campaign (Lefer et al.,
27 2010). Additionally, it is worth noting that experiments conducted using pure VOCs (toluene,
28 isoprene, and hexadecane) in place of motor oil VOCs did not result in net HONO production,
29 ruling out these VOCs as potential reactants. These experiments also rule out HONO artifacts from
30 reactions other than (R3). In other words, despite the <10% HNO_3 -to-HONO conversion efficiency
31 we generally observe in the flow-tube system (Rutter et al., 2014), other nitrogen-containing
32 compounds originating from HNO_3 reduction likely did not contribute to HONO production in this
33 system.

34 Table 1 summarizes experimental data for each type of experiment. Mean values are reported for
35 initial HNO_3 concentrations, f_{HONO} , and water vapor mixing ratios with $N \geq 3$. All error bars and
36 uncertainties reported here were propagated from measurement uncertainties, except those for
37 initial HNO_3 concentrations with $N \geq 3$, which are reported as standard deviations from the mean.
38 The measurement uncertainties were larger than the standard deviations for f_{HONO} in most

1 experiment types, indicating high repeatability. Additional information on uncertainty is included
2 in the Supporting Material.

3 The average HONO formation rates are not statistically different (within 1σ) when initial HNO_3
4 concentrations were ~ 400 , $1\ 500$, and $4\ 000$ ppt, suggesting that the 200 - 300 ppt of reactive
5 VOCs previously estimated by Rutter et al. (2014) (assuming a 1-to-1 stoichiometric ratio) remains
6 the limiting factor. The lowest HNO_3 concentrations achieved in these experiments were ~ 400 ppt
7 (by shutting off HNO_3 supply), which likely reflects the presence of HNO_3 in the air source or the
8 desorption of HNO_3 from the supply tubing, since reactor walls were first rinsed with deionized
9 water and baked under UV lights. A regression showing the weak relationship between f_{HONO} and
10 HNO_3 mixing ratio is shown in Figure S1. Because HNO_3 concentrations above 400 ppt do not
11 appear to significantly impact f_{HONO} , all seven HNO_3 experiments were grouped into one base case
12 category (Table 1). This base case and the Houston 2006 average provide the benchmarks for
13 comparison with other experiments (Figure 2).

14 3.2 Temperature

15 Although the mean f_{HONO} value for the combined base case experiments ($T = 25^\circ\text{C}$) was lower than
16 that for other temperatures, the f_{HONO} at 30.0°C and 35.0°C are not statistically different (within
17 1σ) than that of the base case. However, experiments at 20.0°C yielded significantly higher f_{HONO}
18 (above 1σ). This could mean that the reaction rate increases at lower temperatures, but as
19 mentioned previously this dependence may not follow an Arrhenius trend. This trend suggests the
20 possibility that multiple reactions involving different reactive VOCs become more important at
21 various temperatures. Sampling lines were insulated and heated such that HONO wall losses
22 would be as small as possible, but it should be noted that any bias due to wall losses would likely
23 decrease f_{HONO} at lower temperatures. The enhanced rate at lower temperatures could make the
24 proposed reaction mechanism even more important at night.

25 3.3 NH_3

26 The presence of NH_3 had no observable impact on the reaction. Nitric acid concentrations were at
27 $\sim 3\ 500$ ppt before NH_3 was introduced. After addition of NH_3 , the system equilibrated at $118.0 \pm$
28 2.0 ppb NH_3 and 680 ± 52 ppt HNO_3 . The formation of NH_4NO_3 and its subsequent partitioning into
29 the solid phase is the likely cause for the observed consumption of HNO_3 ; any NH_4NO_3 particles
30 formed would be filtered prior to entering the MC/IC. The f_{HONO} for these experiments also were
31 similar to the base case, likely because HNO_3 was still in excess compared to the VOCs. This
32 indicates that the neutralization reaction between NH_3 and HNO_3 does not directly interfere with
33 the HONO formation reaction beyond the competition for HNO_3 . Consistent with the experiments
34 under varying HNO_3 levels, a lower f_{HONO} is not observed due to the decrease in HNO_3 .

35 3.4 UV Light

36 When UV lights were turned on prior to experiments, a constant photolytic source of HONO from
37 HNO_3 was observed, contributing to background HONO levels (net production of ~ 226 ppt or ~ 5.42

1 ppb hr⁻¹) in the reactor. Several sources could explain this HONO production, for example direct
2 photolysis of HNO₃ sorbed on the reactor walls (Zhou et al., 2003) or from photolysis of
3 nitrophenols (Bejan et al., 2006) that could be present in lubricating oil. We do not have the
4 capability to isolate these sources, but they are not expected to bias f_{HONO} as defined here because
5 formation rates are calculated using a step change in HONO when VOCs were removed during an
6 experiment (Equation (1)). In other words, the HONO formation observed when VOCs were
7 introduced under UV irradiation occurs above and beyond the background photolytic sources.

8 The observed average $f_{HONO,obs}$ under UV irradiation of 0.29 ± 0.17 ppb hr⁻¹ was obtained using the
9 change in HONO levels when VOCs were removed, similar to other experiments. However,
10 according to a simplified mass balance (Equation (2)), the actual HONO production rate ($f_{HONO,UV}$)
11 must correct for photolytic losses of HONO generated when VOCs were present to react with
12 HNO₃:

$$13 \quad f_{HONO,UV} = f_{HONO,obs} + J_{HONO} ([HONO]_{UV+VOCs} - [HONO]_{UV}) \quad \text{Equation (2)}$$

14 where J_{HONO} is the photolysis rate of HONO, and the term in brackets represents the difference in
15 measured HONO mixing ratios with and without VOCs when the lights are illuminated. A
16 spectroradiometer was not available to determine J_{HONO} . In Equation (2), an average J_{HONO} value of
17 $1.75 \times 10^{-3} \text{ s}^{-1}$ was used. This value was derived from an average of measured ambient noon-time
18 J_{HONO} ($1.75 \times 10^{-3} \text{ s}^{-1}$ (Alicke et al., 2003) and $1.60 \times 10^{-3} \text{ s}^{-1}$ (Lee et al., 2013)) and J_{HONO} estimated
19 using the method from Kraus and Hofzumahaus (1998) ($1.90 \times 10^{-3} \text{ s}^{-1}$) from NO₂ photolysis rates
20 reported in an environmental chamber (Nakao et al., 2011) that utilized the same model of lights
21 as this study. When corrected, the average $f_{HONO,UV}$ is 0.37 ± 0.17 ppb hr⁻¹ (Table 1 and Figure 2).
22 However, the J_{HONO} used here is likely much higher than the actual value from only four 40W UV
23 lights, indicating that the $f_{HONO,UV}$ is likely an upper bound. To further test the uncertainty, the
24 estimated value of J_{HONO} used was adjusted by factors of 0.5 and 2 to provide a range of $0.33 \pm$
25 0.17 to 0.44 ± 0.17 ppb hr⁻¹ for the potential average $f_{HONO,UV}$ values.

26 Although $f_{HONO,UV}$ is within the uncertainty range of the base case f_{HONO} , it is likely that the reported
27 $f_{HONO,UV}$ represents an upper bound and that the UV wavelengths studied here could directly
28 interfere with the reduction reaction of HNO₃ to HONO. One explanation for this observation is
29 that under UV irradiation, relevant organic compounds undergo oxidation by radicals formed in
30 the reactor (Atkinson, 2000) or are photolyzed directly. This could alter the reactivity of the VOCs
31 or reduce the total concentration of reactive VOCs available for reaction, hence slowing the overall
32 reaction rate. This and additional tests (Support Material) support the hypothesis that VOCs are
33 the limiting reactants in the reaction proposed here.

34 **3.5 Mineral Dust Aerosol Surfaces**

35 Neither carboxylated-SiO₂ nor Al₂O₃ particles (at concentrations of $\sim 1600 \text{ \#/cm}^3$) yielded
36 significantly different f_{HONO} (within 1σ) than the base case (Figure 2). The slight decrease observed
37 is counterintuitive if the surfaces are expected to enhance the reaction, indicating that the
38 surfaces are potential minor loss sites for the reactive VOCs involved or for the HONO produced

1 (Romanias et al., 2012). This further affirms the probability that a surface is not required to
2 convert HNO₃ to HONO via the proposed pathway.

3 **4. Conclusions**

4 Estimates of base case (25°C, ~20% RH) f_{HONO} derived from the reduction of HNO₃ by VOCs agree
5 well with data from a 2006 field study in Houston (Ziemba et al., 2010) during which
6 enhancements in HONO during morning rush hour were observed. The hypothesized reaction (R3)
7 studied here could have been the main HONO source during the HONO formation events.

8 The HONO formation rate was relatively enhanced (~1.0 ppb hr⁻¹) at a lower temperature of ~20°C
9 but statistically the same (~0.6 ppb hr⁻¹) in experiments at 25, 30 and 35°C. The assumption that
10 multiple reactive components of the VOCs react with HNO₃ is supported by this observation, and
11 the relative importance of each reactive species in the reaction may vary with temperature. The
12 reaction rate is independent of initial HNO₃ concentration (> 400 ppt), suggesting that the
13 concentration of reactive VOCs was the limiting factor. However, future work testing this reaction
14 under HNO₃ concentrations < 400 ppt may provide insights into its relevance in cleaner
15 environments. Ammonia gas consumed HNO₃ in the reactor (down to 680 ppt) but did not have a
16 direct impact on the HONO formation reaction, providing further evidence that the rate is limited
17 by the availability of VOCs in the experimental system. The $f_{HONO,UV}$ from (R3) was likely impeded
18 by UV irradiation. Possible explanations for this observation include the photolysis/deactivation of
19 the reactive VOCs involved in (R3) or the direct interference of UV light on (R3). Nonetheless, this
20 observation must be confirmed by conducting a similar flow-tube study that focuses on
21 constraining the reactive VOCs involved and quantifying HONO photolysis rates. The test of
22 multiple atmospherically-relevant particle surfaces confirmed that the reaction proposed here
23 does not require surfaces to proceed, despite the correlation that was observed in Houston in
24 2006 (Ziemba et al., 2010). Given the uncertainties, we observe substantial percentage changes in
25 f_{HONO} between the base case and the 20°C and UV experiments, even when compared to the
26 change when RH was varied from the base case to 1% or 50% in Rutter et al. (2014). The reduced
27 sensitivity of f_{HONO} to other environmental variables tested here is also an important finding,
28 especially in future modelling work aiming at incorporating this new HONO source to existing
29 atmospheric models.

30 The HONO formation process studied here is likely homogeneous, but the results presented here
31 do not rule out the possibility of a heterogeneous reaction pathway occurring in the atmosphere.
32 Also, it is important to note that the net production of HONO observed in the UV experiments is in
33 addition to production by background photolytic reactions that appear to be occurring on the wax-
34 coated tube walls.

35 The gas-phase conversion of HNO₃ to HONO has significant air quality implications due to the
36 “renoxification” of less reactive HNO₃ into more reactive HONO and should be tested in future
37 modeling and field efforts. This pathway proceeds rapidly in the laboratory when compared with
38 previously identified mechanisms (Table S3) and could potentially be an important source of
39 HONO in the lower atmosphere (2nd order rate constant ~1.0 x 10⁻⁷ ppt⁻¹ s⁻¹ estimated in Gall et al.
40 (2015), in revision for *Atmospheric Environment*). Its role in HONO production aloft (synonymous

1 to the unknown gas-phase HONO source proposed by Li et al. (2014)) cannot yet be ruled out and
2 should be evaluated in future work. In addition to their direct impact on O₃ formation and
3 secondary organic aerosol formation, VOCs could also regulate the oxidative capacity of the
4 atmosphere through the redox reaction studied here. These different processes have significant
5 implications in terms of regional and global air quality. Hence, future experimental work focusing
6 on the quantification of individual reactive components of the VOCs (e.g. utilizing mass
7 spectrometry techniques coupled with proton transfer reaction or gas chromatography) that were
8 involved in the reaction studied here (under varying environmental conditions) would allow
9 detailed characterization of the HONO formation mechanism(s) and determination of reaction
10 yields. Once the HONO formation reaction mechanism is well characterized, parameterizing the
11 reaction would allow improvements in existing O₃ and PM prediction models.

12 **Acknowledgements**

13 We acknowledge financial support from the National Aeronautics and Space Administration (NASA
14 Grant #NNX09AE26G S04). Ammonia measurements were supported by the Mid-InfraRed
15 Technologies for Health and the Environment (MIRTHE) Center and National Science Foundation
16 under grant No. EEC-0540832; Dan Campbell assisted in the ammonia experiments.

17 **Supporting Material Available**

18 Additional information and experiments (Text 1), uncertainty calculations (Text 2), least squares
19 linear regression between f_{HONO} and initial HNO₃ concentration (Figure S1), the blend of engine oils
20 used to generate the VOCs (Table S1), detailed measurement uncertainties and propagated errors
21 in experiments (Table S2), estimated formation rates of previously proposed HONO sources (Table
22 S3). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

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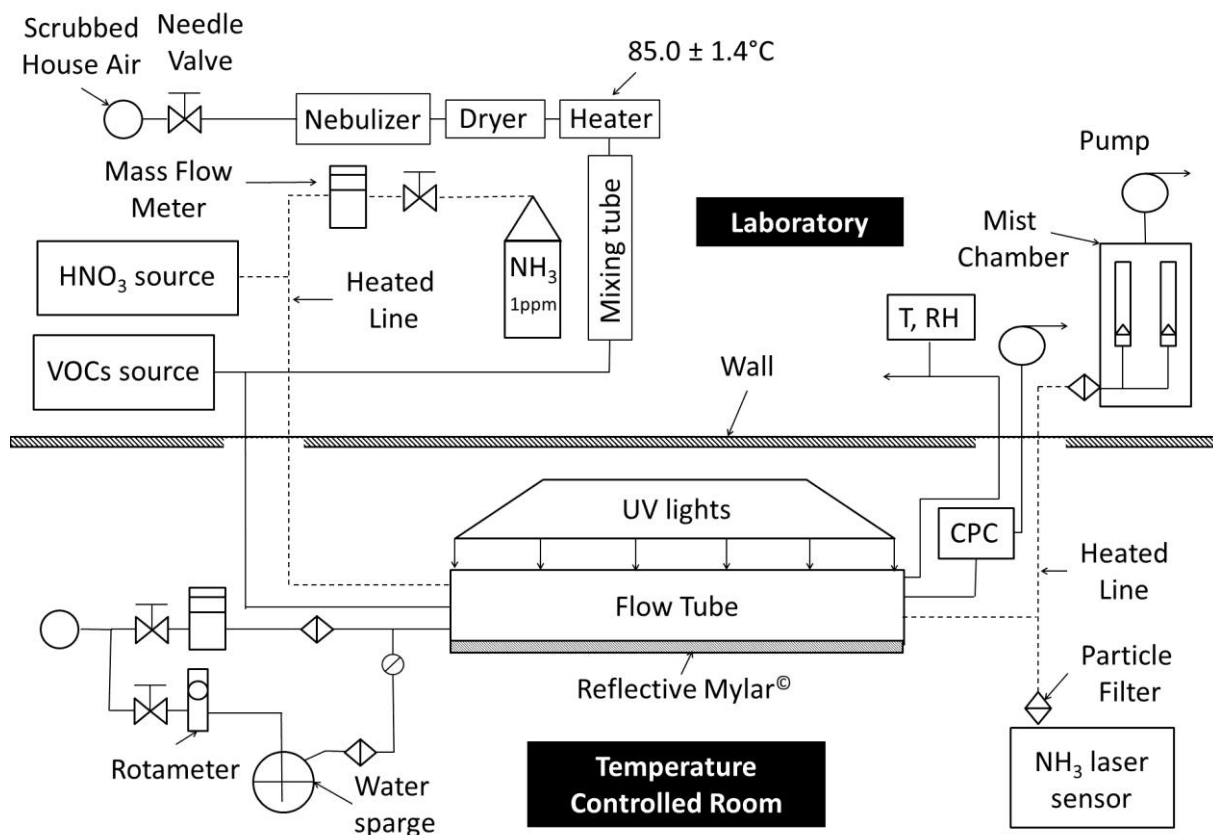
1 **Figure and Table Captions**

2 **Figure 1.** Flow diagram of the flow-tube system and instrumentation. Dashed lines represent
3 heated lines for the flow of low-volatility gases (CPC = condensation particle counter).

4 **Figure 2.** Average HONO formation rates (with error bars) for each experimental category and
5 comparison to the base case (25.0°C and ~20.0% RH without the addition of NH₃, dust particles, or
6 UV irradiation) and field results from Ziemba et al. (2010). HighN, MedN, and LowN represent
7 experiments with high HNO₃, medium HNO₃, and low HNO₃, respectively, and are combined to
8 generate the average base case output. The average HONO formation rate for UV experiments
9 was corrected for photolytic HONO losses (see Section 3.4).

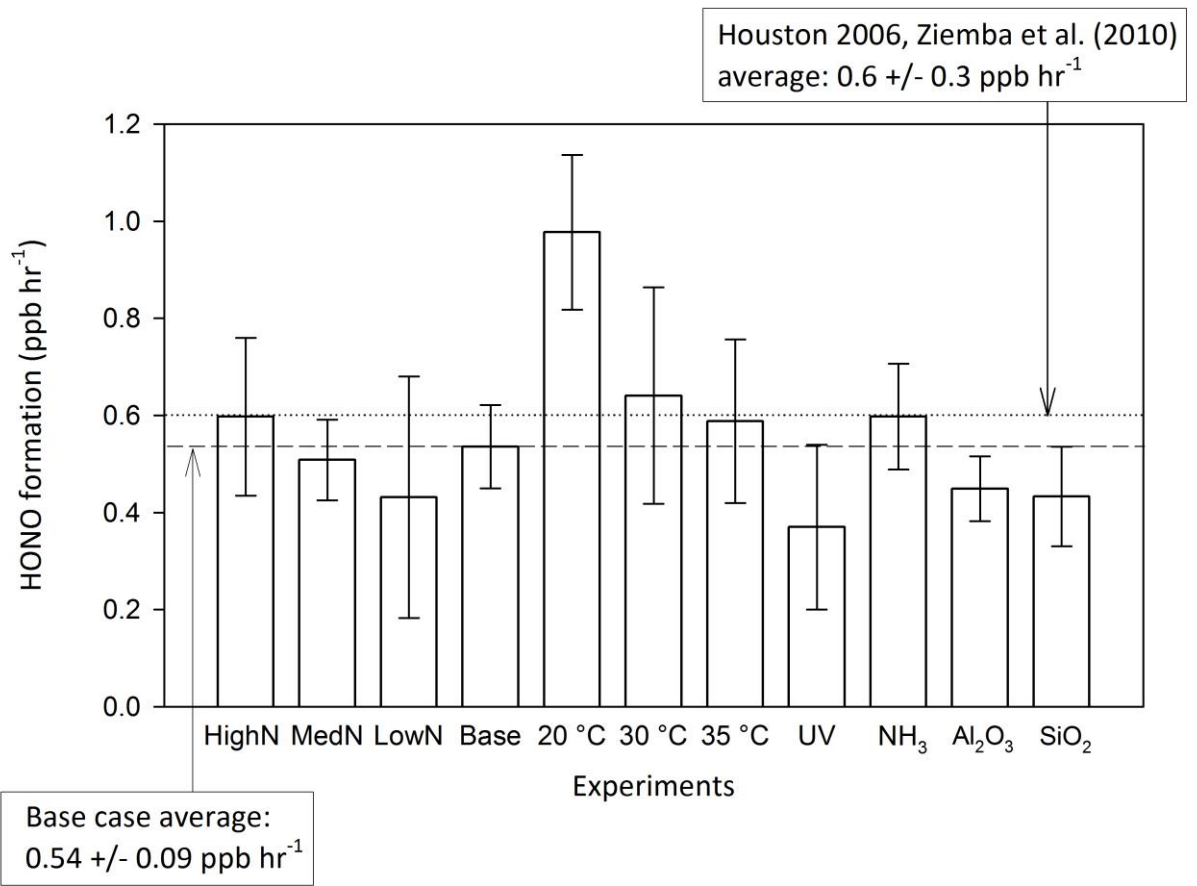
10 **Table 1.** Summary of experimental conditions and average HONO formation rates.

11 **Figures**



12

13 **Figure 1.**



1
2 **Figure 2.**
3

1 Tables

Table 1.

Experiment	Initial HNO ₃ (ppt)	Unc/stdev (ppt)	N ^a	f_{HONO} (ppb/hr)	Unc /stdev (ppb/hr)	Water Vapor Mixing ratio (%)	Notes
Base case, High HNO ₃	3 980	936	3	0.60	0.16	0.67	T = 25.0°C
Base case, Medium HNO ₃	1 522	159	3	0.51	0.08	0.63	T = 25.0°C
Base case, Low HNO ₃	399	53	1	0.43	0.25	0.58	T = 25.0°C
Base case, all HNO ₃ levels	2 415	1 613	7	0.54	0.09	0.64	T = 25.0°C
T = 20.0 °C	2 763	52	3	0.98	0.16	0.86	
T = 30.0 °C	4 344	361	4	0.64	0.22	0.73	
T = 35.0 °C	3 755	474	4	0.59	0.17	0.98	
UV Irradiation	3 405	451	3	0.37	0.17	0.59	Corrected for UV losses
Ammonia	680	52	3	0.60	0.11	0.73	NH ₃ = 118.0 ± 2.0 ppb
Alumina aerosol	3 356	346	3	0.45	0.07	0.61	Average count = 1600 #/cm ³
Silica-COOH aerosol	3 443	85	3	0.43	0.10	0.60	Average count = 1600 #/cm ³

^a N = number of experiments conducted

2

3

1 **Supporting Material**

2 **Impact of Environmental Variables on the Reduction of Nitric Acid by Proxies for Volatile Organic**
3 **Compounds Emitted by Motor Vehicles**

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19

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8 Table S1. The blend of engine oils used to generate the VOCs

9 S5

10 Table S2. Detailed measurement uncertainties and propagated errors in experiments

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12 Table S3. Estimated rates of previously identified HONO formation mechanisms

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14 References

15 S9

16 **1. Additional information and experiments**

17 The reader is referred to section 2.4 of our previous manuscript (Rutter et al., 2014) for a detailed
18 discussion of the choice of engine oil VOCs used as proxies for vehicular emissions. Background
19 levels of HONO (~30 ppt) and HNO_3 (~400 ppt) in the reactor were achieved upon rinsing the
20 system with water and baking with UV lights for ~8 hours.

21 Experiments conducted using several pure organic compounds (such as toluene, isoprene, and
22 hexadecane) instead of engine oil VOCs did not result in HONO production.

23 Three experiments were conducted at $T = 20\text{ }^\circ\text{C}$ and by diluting the source of VOCs with clean air
24 prior to injection to the flow-tube reactor (other conditions were identical to the $T = 20\text{ }^\circ\text{C}$
25 experiments). The diluted concentration of reactive VOCs in the reactor was estimated based on
26 mass balance to be ~55% of the nominal concentration used. The dilution of VOCs resulted in f_{HONO}

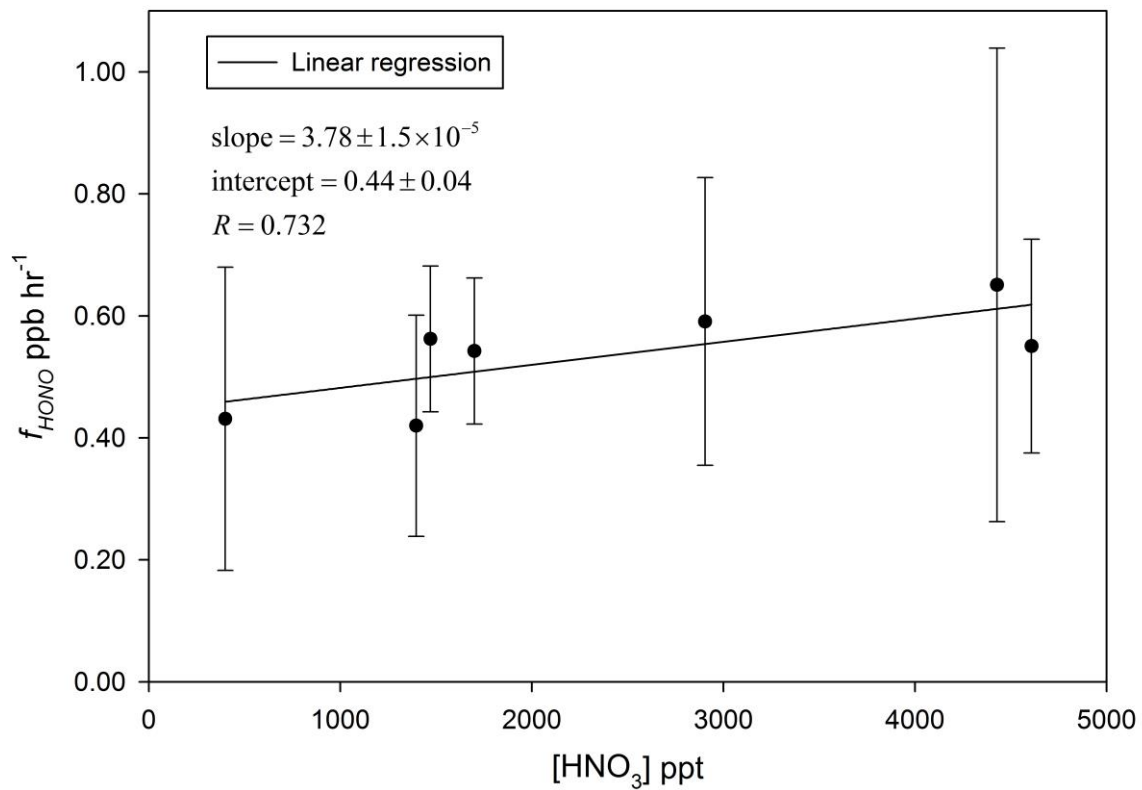
1 of 0.72 ± 0.22 ppb hr⁻¹, which is lower when compared with f_{HONO} of 0.96 ± 0.18 ppb hr⁻¹ for the
2 nominal T= 20°C experiments (Table 1). This comparison provides supporting evidence that the
3 concentration of VOCs was the limiting factor for the reaction discussed here. However, these
4 experiments were not used in direct comparison with the other experimental categories because
5 two variables (temperature and concentration of VOCs) were changed simultaneously.

6 Tests were also conducted to rule out heterogeneous reactions in the flow tube reactor, by
7 measuring f_{HONO} under varying residence times while keeping other parameters constant. The f_{HONO}
8 for different residence times were statistically similar, which lends support to our case that HONO
9 formation occurred predominantly in the gas phase.

10 **2. Uncertainty calculations**

11 Weekly calibrations for the mist chamber/ion-chromatography (MC/IC) were conducted to
12 minimize systematic errors in HONO mixing ratio measurements ([HONO] in ppt). The overall
13 measurement uncertainties in $[HONO]_t$ and $[HONO]_o$ in Equation (1) were estimated from the
14 standard deviation of 1-hour averages of steady-state [HONO] (immediately prior to and after the
15 removal of VOCs). These uncertainties were propagated to the f_{HONO} “Unc” values for individual
16 experiments as shown in Table S2. When calculating the mean f_{HONO} value for each experimental
17 category, the individual uncertainties are again propagated to give an estimate of the uncertainty
18 in the averaged f_{HONO} value (“Prop”). These propagated measurement uncertainties are larger than
19 the spread in f_{HONO} values for each category (standard deviation of the average, “Stdev”), indicating
20 good repeatability. The same procedures were used to calculate initial [HNO₃] and [HONO] values
21 (also shown in Table S2). The larger of either the ‘Stdev.’ or ‘Prop.’ values for initial [HNO₃] or f_{HONO}
22 were used to represent their respective uncertainty ranges in Table 1 and Figure 2 in the main text.

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2 **Figure S1.** Least squares linear regression between f_{HONO} and initial HNO_3 concentration from
 3 seven experiments conducted at varying HNO_3 concentrations. The slope and intercept are
 4 reported with standard error estimated from the linear regression and have units of $ppb\ hr^{-1}\ ppt^{-1}$
 5 and $ppb\ hr^{-1}$ respectively.

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Table S1. The blend of engine oils used to generate the VOCs in this study (adapted from Rutter et al. (2014))

Name	Grade	Intended Engine Type	Volume (ml)
Castrol GTX	5W-30	Gasoline	25
Castrol GTX	10W-30	Gasoline	25
Mobil 1 High Mileage	5W-30	Gasoline	25
Mobil 1 High Mileage	10W-30	Gasoline	25
Mobil 1 Extended Performance	5W-20	Gasoline	25
Valvoline Premium Conventional	5W-30	Gasoline	25
Valvoline Premium Conventional	10W-30	Gasoline	25
Quaker State Advanced Durability	5W-30	Gasoline	25
Quaker State Advanced Durability	10W-30	Gasoline	25
Pennzoil Active	5W-30	Gasoline	25
Pennzoil Active	10W-30	Gasoline	25
Pennzoil Active	5W-20	Gasoline	25
Castrol GTX Diesel	15W-40	Diesel	115

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Table S2. Detailed measurement uncertainties and propagated errors in experiments. ‘Unc’ values for individual experiments represent errors propagated from measurement uncertainties. Rows denoted with ‘Stdev.’ refer to standard deviations of the calculated average values; rows denoted with ‘Prop.’ refer to the propagated errors of the average.

Expt No.	Category	Initial [HNO ₃] (ppt)	Unc type	Unc (ppt)	Initial [HONO] (ppt)	Unc (ppt)	f_{HONO} (ppb hr ⁻¹)	Unc (ppb hr ⁻¹)
1	Base case, High HNO ₃	4608		77	63.7	1.5	0.55	0.18
2	Base case, High HNO ₃	4428		30	67.4	0.8	0.65	0.39
3	Base case, High HNO ₃	2904		29	70.5	1.9	0.59	0.24
Avg	Base case, High HNO ₃	3980	Stdev.	936	67.2	3.4	0.60	0.05
			Prop.	29		0.8		0.16
4	Base case, Med HNO ₃	1471		11	40.6	0.7	0.56	0.12
5	Base case, Med HNO ₃	1700		26	39.8	1.1	0.54	0.12
6	Base case, Med HNO ₃	1395		8	43.9	1.0	0.42	0.18
Avg	Base case, Med HNO ₃	1522	Stdev.	159	41.4	2.2	0.51	0.08
			Prop.	10		0.5		0.08
7	Base case, Low HNO ₃	399		53	47.2	1.9	0.43	0.25
Avg	Base case, all HNO ₃	2415	Stdev.	1613	53.3	13.4	0.54	0.08
			Prop.	15		1.2		0.09
8	T = 20.0 °C	2704		35	45.2	0.9	1.14	0.20
9	T = 20.0 °C	2740		27	46.2	1.7	0.93	0.23
10	T = 20.0 °C	2785		79	51.1	1.1	0.93	0.22
11	T = 20.0 °C	2823		55	58.5	2.1	0.91	0.30
Avg	T = 20.0 °C	2763	Stdev.	52	50.3	6.1	0.98	0.11
			Prop.	35		1.0		0.16
12	T = 30.0 °C	4741		22	75.4	4.2	0.78	0.41
13	T = 30.0 °C	4505		24	95.2	3.5	0.36	0.35
14	T = 30.0 °C	4227		27	75.5	1.9	0.78	0.30
15	T = 30.0 °C	3904		20	76.8	2.5	0.65	0.27
Avg	T = 30.0 °C	4344	Stdev.	361	80.7	9.7	0.64	0.20
			Prop.	16		2.1		0.22
16	T = 35.0 °C	4389		21	104.3	3.0	0.59	0.27
17	T = 35.0 °C	3838		24	71.0	2.6	0.53	0.37
18	T = 35.0 °C	3448		25	69.1	1.5	0.77	0.17
19	T = 35.0 °C	3343		42	76.2	1.1	0.47	0.13
Avg	T = 35.0 °C	3755	Stdev.	474	80.2	16.4	0.59	0.13
			Prop.	19		1.5		0.17
20	UV Irradiation	2886		71	315.1	2.4	0.30	0.24
21	UV Irradiation	3704		59	263.4	2.2	0.33	0.29
22	UV Irradiation	3625		21	251.1	3.7	0.24	0.33
Avg	UV Irradiation (uncorrected)	3405	Stdev.	451	276.5	34.0	0.29	0.04
			Prop.	32		1.6		0.17
	UV Irradiation		Prop.				0.37	0.17

(corrected, Eq. (2))

Table S1 (continued)

Expt No.	Category	Initial [HNO ₃] (ppt)	Unc type	Unc (ppt)	Initial [HONO] (ppt)	Unc (ppt)	<i>f</i> _{HONO} (ppb hr ⁻¹)	Unc (ppb hr ⁻¹)
23	Ammonia	3370		53	95.4	1.6	0.58	0.17
24	Ammonia	3717		71	96.1	1.4	0.61	0.20
25	Ammonia	3909		66	97.9	1.1	0.60	0.20
Avg	Ammonia	3666	Stdev.	273	96.5	1.3	0.60	0.01
			Prop.	37		0.8		0.11
26	Alumina aerosol	3565		29	88.5	0.5	0.40	0.14
27	Alumina aerosol	2956		116	92.7	0.8	0.57	0.11
28	Alumina aerosol	3546		46	81.6	0.6	0.38	0.08
Avg	Alumina aerosol	3356	Stdev.	346	87.6	5.6	0.45	0.10
			Prop.	43		0.4		0.07
29	Silica aerosol	3541		24	90.0	0.4	0.36	0.08
30	Silica aerosol	3393		15	91.3	1.2	0.38	0.27
31	Silica aerosol	3394		18	89.6	0.5	0.56	0.13
Avg	Silica aerosol	3443	Stdev.	85	90.3	0.9	0.43	0.11
			Prop.	11		0.5		0.10

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Table S3. Estimated rates of previously identified HONO formation mechanisms using observed or typical ambient parameters. Parameters used in the source strength calculations are included below.

Source rank	HONO source mechanism	Estimated source strength (ppb hr ⁻¹)	Input parameters	Daytime/ Nighttime	Reference
1	Gas-phase source that scales with J_{HONO}	0.69	$S_{\text{HONO}}, J_{\text{HONO}}$	Day	<i>Li et al. (2014)</i>
2	Homogeneous source (HNO ₃ and VOCs)	0.54	-	Day/Night	<i>This study</i>
3	Photolysis of surface-adsorbed HNO ₃ (scaled by [HNO ₃])	0.54	$P_{\text{HNO}_3}, [\text{HNO}_3]$	Day	<i>Zhou et al. (2003)</i>
4	Reaction between OH and NO	0.33	$k_{\text{OH-NO}}, [\text{OH}], [\text{NO}]$	Day	<i>Atkinson et al. (2004)</i>
5	NO ₂ surface production	0.004	$\gamma_{\text{NO}_2}, h, [\text{NO}_2]$	Day/Night	<i>VandenBoer et al. (2013)</i>
6	NO ₂ hydrolysis on aerosol surface	0.0002	$k_{\text{NO}_2}, S/V, [\text{NO}_2]$	Day/Night	<i>Kurtenbach et al. (2001)</i>

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Parameter	Symbol	Units	Value	Reference
HONO production rate	S_{HONO}	ppt s h ⁻¹ × J_{HONO}	4.05E+05	<i>Li et al. (2014)</i>
Ambient noon-time HONO photolysis rate	J_{HONO}	s ⁻¹	1.70E-03	(<i>Alicke et al. (2003); Lee et al. (2013)</i>)
HONO production (700 ppt HNO ₃)	P_{HNO_3}	ppb hr ⁻¹	1.50E-01	<i>Zhou et al. (2003)</i>
Rate constant	$k_{\text{OH-NO}}$	[N ₂] cm ³ molecule ⁻¹ s ⁻¹	7.52E-31	<i>Atkinson et al. (2004)</i>
NO ₂ uptake coefficient	γ_{NO_2}	-	2.00E-06	<i>VandenBoer et al. (2013)</i>
Rate constant	k_{NO_2}	(S/V) min ⁻¹ m ⁻¹	3.00E-03	<i>Kurtenbach et al. (2001)</i>
Experimental nitric acid levels	[HNO ₃]	ppt	2500	<i>This study</i>
12-hr daytime hydroxyl radical	[OH]	ppt	0.08	<i>Atkinson (2000)</i>
Assumed daytime nitrogen oxide	[NO]	ppb	2.5	-
Assumed daytime nitrogen dioxide	[NO ₂]	ppb	5	-
Daytime boundary layer height, Houston	h	m	400	<i>Banta et al. (2005)</i>
Median aerosol surface area, Houston	S/V	mm ² cm ⁻³	232	(<i>Ziemba et al. (2010)</i>)

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