**Supplementary information for**

**Potential interferences in photolytic nitrogen dioxide converters for ambient air monitoring: Evaluation of a prototype**

Nick Jordan, Natasha M. Garner, Laura C. Matchett,a Travis W. Tokarek, and Hans D. Osthoff\*

Department of Chemistry, 2500 University Drive NW, University of Calgary, Calgary, AB T2N 1N4, Canada

Charles A. Odame-Ankrah, Charles E. Grimm, Kelly N. Pickrell, Christopher Swainson, and Brian W. Rosentreter

Global Analyzer Systems Ltd., #5, 1411 – 25th Avenue N.E., Calgary AB T2E 7L6, Canada

\* Author to whom correspondence should be addressed  
email [hosthoff@ucalgary.ca](mailto:hosthoff@ucalgary.ca), phone 403-220-8689

anow at: Department of Chemistry, 11227 Saskatchewan Drive, University of Alberta, Edmonton, AB T6G 2G2, Canada

For the *Journal of the Air & Waste Management Association*

April 17, 2020

Experimental setup

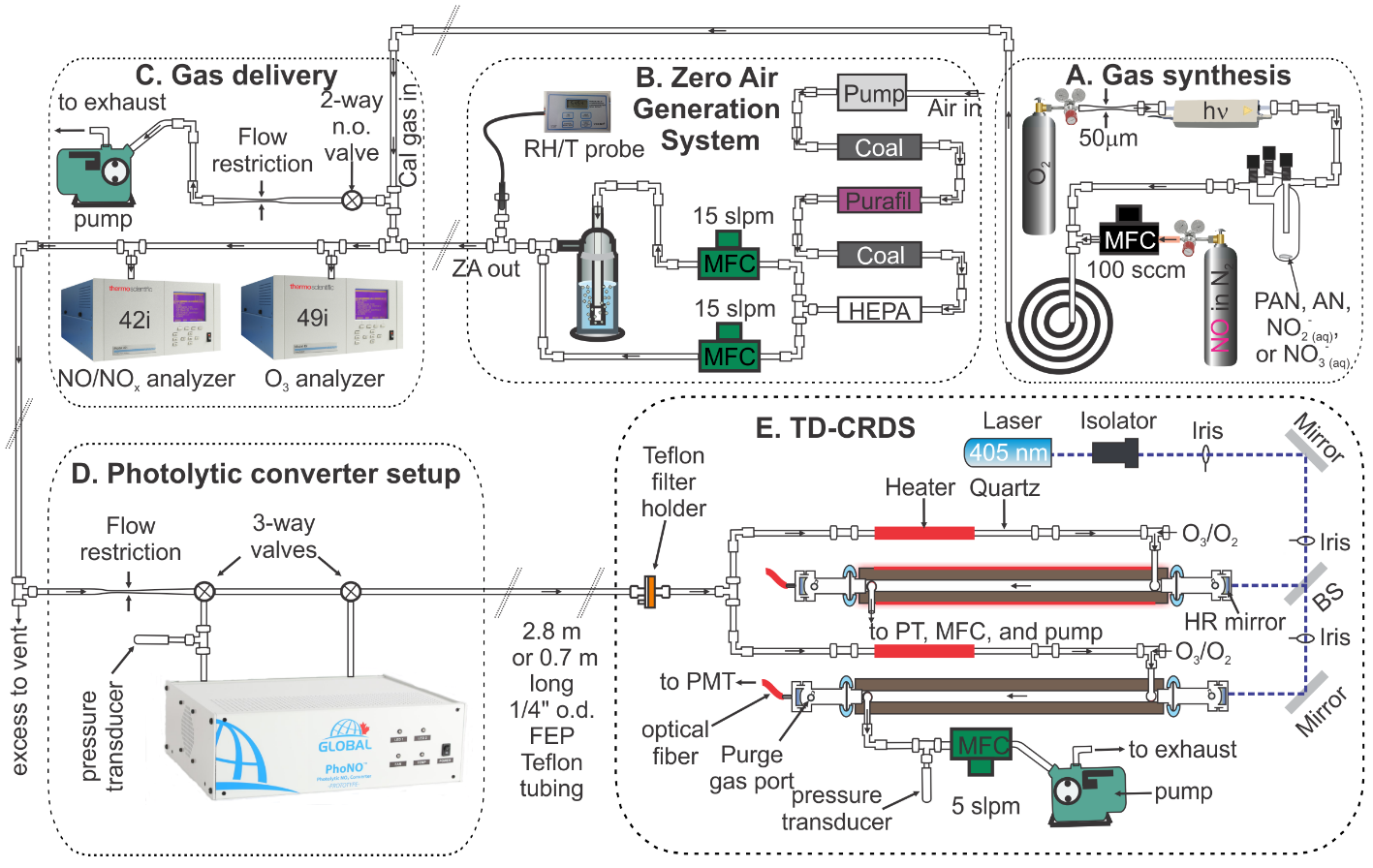


Figure S1. Experimental setup. MFC = mass flow controller; slpm = standard liter per minute; RH/T = relative humidity and temperature; ZA = zero air; n.o. = normally open; FEP = fluorinated ethylene propylene; PMT = photomultiplier tube; PT = pressure transducer; HR = high reflectivity; BS = beam splitter

Generation and delivery of NOz species

*Generation of gas streams containing PAN.* Peroxyacetic nitric anhydride was synthesized by combining 2.5 mL of 32% peracetic solution (Sigma-Aldrich) with 20 mL of tridecane (Sigma-Aldrich) in a 100 mL round bottom flask, which was cooled externally using an ice-water bath. Approximately 5 mL of pre-cooled, concentrated H2SO4 (Sigma-Aldrich, fuming) were added dropwise to the stirred solution, followed by dropwise addition of ice-cold, concentrated HNO3 (Sigma-Aldrich, ACS reagent, 90%). After 15 min, the mixture was transferred to a pre-cooled separatory funnel. The organic layer was washed with three 50 mL batches of ice-cold deionized water and dried with anhydrous MgSO4 (EMD). Aliquots of PAN in tridecane were filtered into 2 mL centrifuge vials (VWR), which were stored in a freezer until use. To generate gas streams containing PAN, the contents of a vial containing PAN in tridecane were transferred to a 3-neck flask cooled externally with water-ice and eluted using a stream of ~100 sccm oxygen (Praxair).[1](#_ENREF_1)

*Generation of gas streams containing HONO.* Mixtures of HONO in air were generated by placing 100 mg of sodium nitrite (Sigma-Aldrich) and 5 mL of a solution buffered to pH 3.74 using sodium oxalate / oxalic acid in a 3-neck flask. The head space of this solution initially contained high concentrations of NOx, which was removed through continuous flushing with N2 gas over periods of several days and by keeping the solution in the dark.

*Generation of gas streams containing isopropyl nitrate (IPN)*. Isopropyl nitrate was purchased from Sigma-Aldrich and used as received. A permeation source was constructed by filling a "low emission" polytetrafluoroethylene (PTFE) permeation tube (Chromatographic Specialties) with IPN and sealing both ends using solid PTFE plugs that were externally compressed using stainless steel rings.[2](#_ENREF_2) The permeation tube was place inside 3/4" (1.9 cm) o.d. FEP Teflon™ tubing, which was continuously flushed with ~100 sccm oxygen (Praxair). This assembly was operated at room temperature but could be externally heated if a higher emission rate was desired.

*Generation of gas streams containing HNO3*. A permeation tube filled by a commercial vendor (KIN-TEK Analytical) with 68% HNO3 was placed inside a flow chamber (VICI Dynacalibrator) heated to a temperature of 60.0 °C and operated at a flow of 0.15 Liters per minute. Its output was immediately diluted in ~100 sccm of oxygen.

Box model simulations

A macro was written in Igor Pro 6 (Wavemetrics, Lake Oswego, Oregon) to rationalize the experiment shown in Figure 5B. The simulation models the chemistry that occurs in a parcel of air as it travels through the photolytic converter and the tubing connected to the analyzer at a mass flow rate of 903 sccm. The reactions are summarized in Table S1. The model assumes a pressure of 420 Torr throughout, a room temperature of 298 K, a temperature of 318 K inside the converter, and *tres* = 3.5 sec, calculated from the inner dimensions of the photolysis cell and volumetric flow rate. Photolysis was assumed to be uniform inside the converter and turned off outside. Simulations were initialized with 21 ppbv NO2 (2.9×1011 molecules cm-3), 79% N2 (1.1×1019 molecules cm-3), 21% O2 (2.8×1018 molecules cm-3), H2O (1×1017 molecules cm-3), CH4 (3×1013molecules cm-3), CO (2×1012 molecules cm-3), and NO mixing ratios of 0, 4, 43, 111, and 194 ppbv (0, 5.6×1010, 6.0×1011, 1.5×1012, and 2.7×1012 molecules cm-3, respectively).

Table S1: Mechanism used in box model simulations. n/a = not applicable. Fc = 0.6 unless noted otherwise.

|  |  |  |  |
| --- | --- | --- | --- |
| **#** | **Reaction** | **Rate constant or expression** | **Ref.** |
| 1 | NO2 + hν → NO + O(3P) | 4.2 sec-1 | n/a |
| 2 | HONO+ hν → HO + NO | 0.137 sec-1 | n/a |
| 3 | O3 + hν → O(3P) + O2 | 1.46×10-4 sec-1 | n/a |
| 4 | O3 + hν → O(1D) + O2 | 5.45×10-10 sec-1 | n/a |
| 5 | O(3P) + O2 (+ M) → O3 (+ M) | ko300=6.0×10-31 cm6 molecule-2 sec-1, n=2.6  k∞300=3.6×10-11 cm3 molecule-1 sec-1, m=0.1 | [3](#_ENREF_3) |
| 6 | O(3P) + O3 → 2O2 | 8.0×10-12×e-2060/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 7 | O(1D) + N2 → O(3P) + N2 | 2.15×10-11×e110/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 8 | O(1D) + O2 → O(3P) + O2 | 3.3×10-11×e55/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 9a | O(1D) + O3 → 2O2 | 1.2×10-10 cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 9b | O(1D) + O3 → 2O(3P) + O2 | 1.2×10-10 cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 10 | O(1D) + H2O → 2 HO | 1.63×10-10×e60/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 11 | NO + O3 → NO2 + O2 | 3.0×10-12×e-1500/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 12 | NO2 + O(3P) → NO + O2 | 1.04×10-11×e210/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 13 | HO + NO (+ M) → HONO (+ M) | ko300=7.0×10-31 cm6 molecule-2 sec-1, n=2.6  k∞300=3.6×10-11 cm3 molecule-1 sec-1, m=0.1 | [4](#_ENREF_4) |
| 14 | HO + NO2 (+ M) → HNO3 (+ M) | ko300= 1.8×10-30 cm6 molecule-2 sec-1, n=3.0  k∞30 = 2.8×10-11 cm3 molecule-1 sec-1, m=0 | [4](#_ENREF_4) |
| 15 | NO + HO2 → NO2 + HO | 3.3×10-12×e270/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 16 | OH + HONO → H2O + NO2 | 1.8×10-11×e-390/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 17 | HO + O3 → HO2 + O2 | 1.7×10-12×e-940/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 18 | HO2 + O3 → HO + 2O2 | 1.0×10-14×e-490/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 19 | HO + HO2 → H2O + O2 | 4.8×10-11×e250/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 20 | NO2 + O3 → NO3 + O2 | 1.2×10-13×e-2450/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 21 | NO + NO3 → 2NO2 | 1.5×10-11×e170/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 22 | NO2 + NO3 (+ M)  → N2O5 (+ M) | ko300=2.4×10-30 cm6 molecule-2 sec-1, n=3.0  k∞300=1.6×10-12 cm3 molecule-1 sec-1, m=‑0.1 | [4](#_ENREF_4) |
| 23 | NO3 + hν → NO2 + O(3P) | 0.149 sec-1 | n/a |
| 24 | N2O5 → NO2 + NO3 | k22 / (5.8×10-27× e10840/T cm3 molecule-1 sec-1) | [4](#_ENREF_4) |
| 25 | HO + CO (+ O2)  → CO2 + HO2 | 1.5×10-13 cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 26 | N2O3 (+ M) → NO + NO2(+ M) | ko=1.9×10-7×(T/300)-8.7 e-4880/T [M] sec-1  k∞=4.7×1015×(T/300)0.4 e-4880/T sec-1 | [5](#_ENREF_5)\* |
| 27 | N2O3 + H2O → 2HONO | 6.29×10-11×e-4470/T cm3 molecule-1 sec-1 | [6](#_ENREF_6) |
| 28 | NO + NO2 (+ M) → N2O3 (+ M) | ko=3.1×10-34×(T/300)-7.7×[M] cm3 molecule-1 sec-1  k∞=7.9×10-12×(T/300)-1.4 cm3 molecule-1 sec-1 | [5](#_ENREF_5)\* |
| 29 | HO + CH4 (+ O2) → CH3O2 + H2O | 2.45×10-12×e-1775/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 30 | CH3O2 + NO (+ O2) → NO2 + HO2 (+ HCHO) | 2.8×10-12×e300/T cm3 molecule-1 sec-1 | [4](#_ENREF_4) |
| 31 | 2NO2 → N2O4 | ko=1.44×10-33×(T/298)-3.8×[M] cm3 molecule-1 sec-1  k∞=1.0×10-12 cm3 molecule-1 sec-1 | [5](#_ENREF_5)\* |
| 32 | N2O4 (+ M) → 2NO2(+ M) | k0=1.3×10-5×(T/300)-3.8×e-6400/T [M]sec-1  k∞=7.7×1015×(T/300)-1.1×e-6460/T sec-1 | [5](#_ENREF_5)\* |
| 33 | N2O4 + H2O → HONO + HNO3 | 4.18×10-10×e-5830/T cm3 molecule-1 sec-1 | [6](#_ENREF_6) |

\* data downloaded from http://iupac.pole-ether.fr/

Interference from selected NOz species.

*Alkyl nitrates*. The ANs are not expected to photodissociate in this wavelength region, but since they are an important component of photochemical smog, their inertness was experimentally verified. In Figure S2, the CRDS sampled 70±1 ppbv of IPN from 19:49 to 19:56, which was quantified by heating the TD-CRDS quartz inlet to 420 °C. The IPN diffusion source co-emitted a small amount (average of 0.455 ppbv) of NOx. When the converter's LEDs were turned on from 19:52 to 19:54, the NOx mixing ratio increased to 0.74±0.12 ppbv. The difference (0.74±0.12 - 0.48±0.10 = 0.26±0.16 ppbv) is of the same magnitude as the UV-induced artifact (0.3±0.1 ppbv, measured at 19:45 - 19:47), indicating there that IPN did not photodissociate to yield NO, as expected.

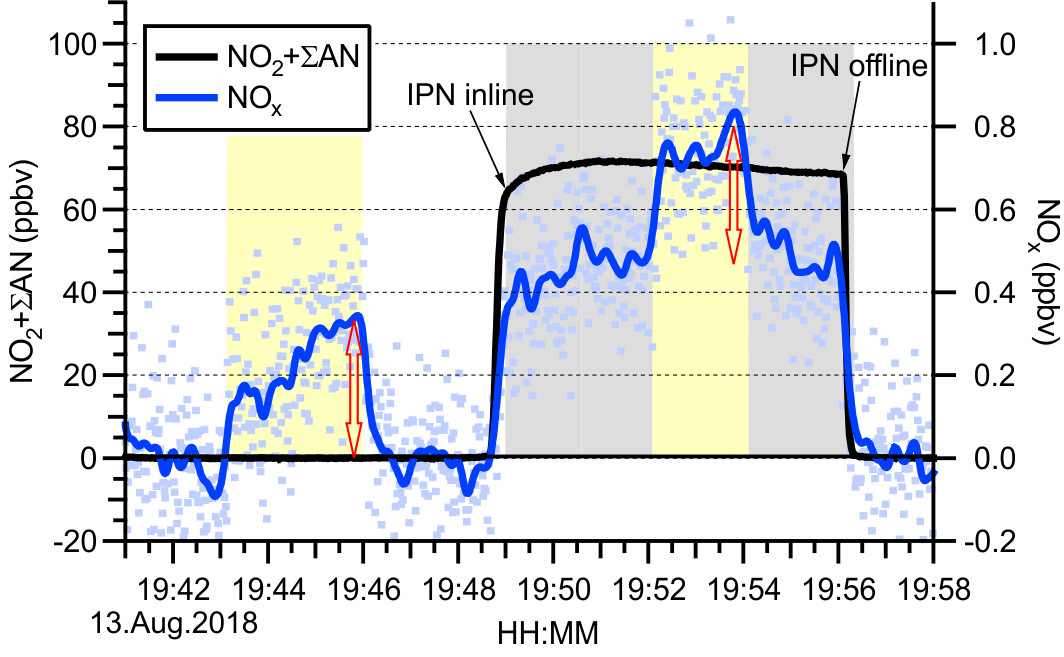


Figure S2. Time series of NO production in zero air and from isopropyl nitrate photolysis. The 1 sec NOx data are shown in light blue. The solid blue line was obtained after applying a 60 sec binomial filter to the 1 sec data. The arrow (shown in red color) indicates the size of the UV artifact. Flow rate = 0.90 slpm. Pressure = 478 Torr.

*Nitrous acid*. As outlined in the main manuscript, HONO is a molecule expected to directly interfere in the photolytic conversion of NO2. Figure S3 shows a time series probing this interference experimentally. About 40% of HONO was expected to convert with the converter residence time set at 3.6 sec, equivalent to a photolysis frequency of 0.14 sec-1 (Table 2). From 18:09 to 18:13, the output of the diffusion source was sampled in parallel by the CEAS (which was teed in prior to the photolytic converter), a regular CRDS (NO2) channel, and a TD-CRDS channel operated at 600 °C and with O3 after the quartz tube to oxidize the thermal dissociation product of HONO, NO, to NO2; this channel corresponds to an NOy measurement.[7](#_ENREF_7) In this example, the diffusion source emitted a mixture of HONO (0.6±0.1 ppbv) and HNO3 (0.5±0.1 ppbv) and a negligible amount of NOx (0.01±0.05 ppbv). Following a brief zeroing period, the two CRDS channels sampled through the converter at 18:15, which was turned on at 18:16:30, while the CEAS continued to sample the test gas mixture entering the photolytic converter. At 18:19, the O3 addition was switched from the NOy to the NO2 channel, converting the latter into a NOx measurement. An average of (0.75±0.05) ppbv of NOx was observed. Subtracting a UV-induced-artifact of ~(0.3±0.1) ppbv (Figure S2) and subtracting the amount of NOx produced from HNO3, calculated assuming that ~14% (see section titled "HNO3" below) of the (0.5±0.1) ppbv HNO3 converted to NOx, or (0.07±0.02) ppbv) suggests that (0.38±0.11) ppbv of NO was produced from HONO, a yield of (63±21)%.

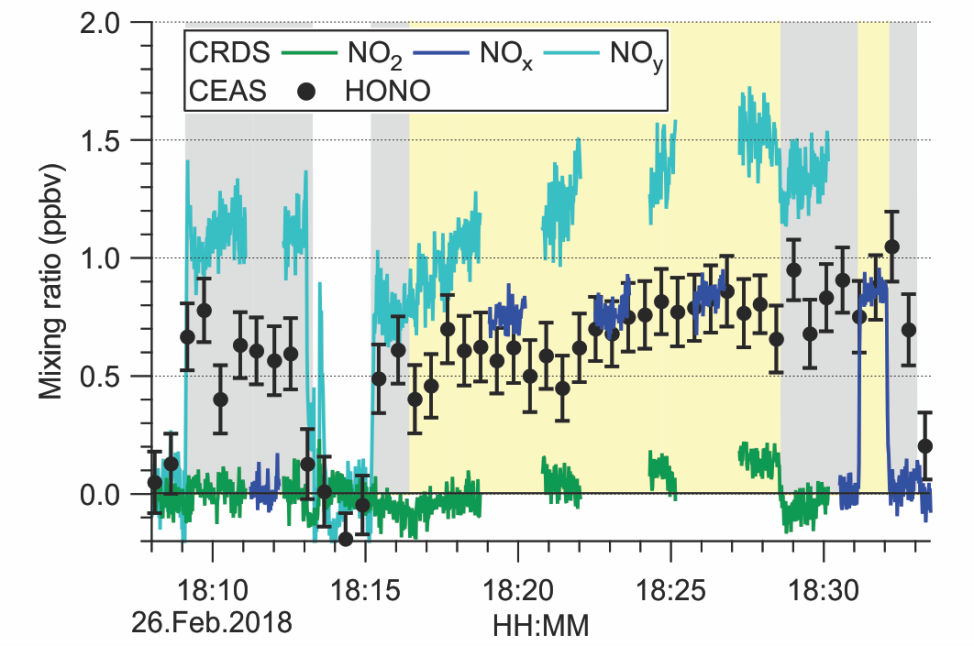


Figure S3. Photochemical conversion of HONO to NO. At 18:09, the CRDS and CEAS sampled the HONO source, which emitted ~0.6 ppbv of HONO (shown in black), ~0.0 ppbv NO2 (shown in green) and NOx (shown in blue), and ~0.5 ppbv of HNO3 (calculated relative to NOy). The instruments sampled zero air from 18:13 to 18:15. At 18:15:15, the CRDS sampled through the converter (Pressure ~580 Torr; residence time ~3.6 sec), which was turned on at 18:16:30.

The experiment shown in Figure S3 was repeated with shorter photolysis residence times. A fit of eq 7 (with *k*[Ox] = 0 sec-1) to a plot of NO against *tres*(not shown) indicates a HONO photolysis frequency of 0.25 sec-1, slightly larger than predicted from the overlap of the LED emission spectrum with the absorption spectrum of HONO.

*PAN*. Reed et al.[8](#_ENREF_8) examined interferences in their photolytic converter and reported thermal dissociation of PAN to NO2, leading to measurement artifacts that are highly elevated in remote environments.

CH3C(O)O2NO2 ⇌ CH3C(O)O2 + NO2 (12)

Hence, the stability of PAN within the converter was investigated. Figure S4 shows a time series of the response to sampling PAN. Here, one of the TD-CRDS quartz inlets was heated to 250 °C; this channel was used to monitor NO2+ΣPAN (shown in red color) [9](#_ENREF_9), while O3 was added to the other CRDS channel which monitored NOx (shown in blue color). Both channels sampled through the converter. After the usual zeroing period, (18.8±0.1) ppbv of PAN were added to the inlet at 22:54. The LEDs were turned on at 22:56. Initially, there was no change, but over time, the observed NO2+ΣPAN mixing ratio decreased, while the NOx mixing ratio increased.

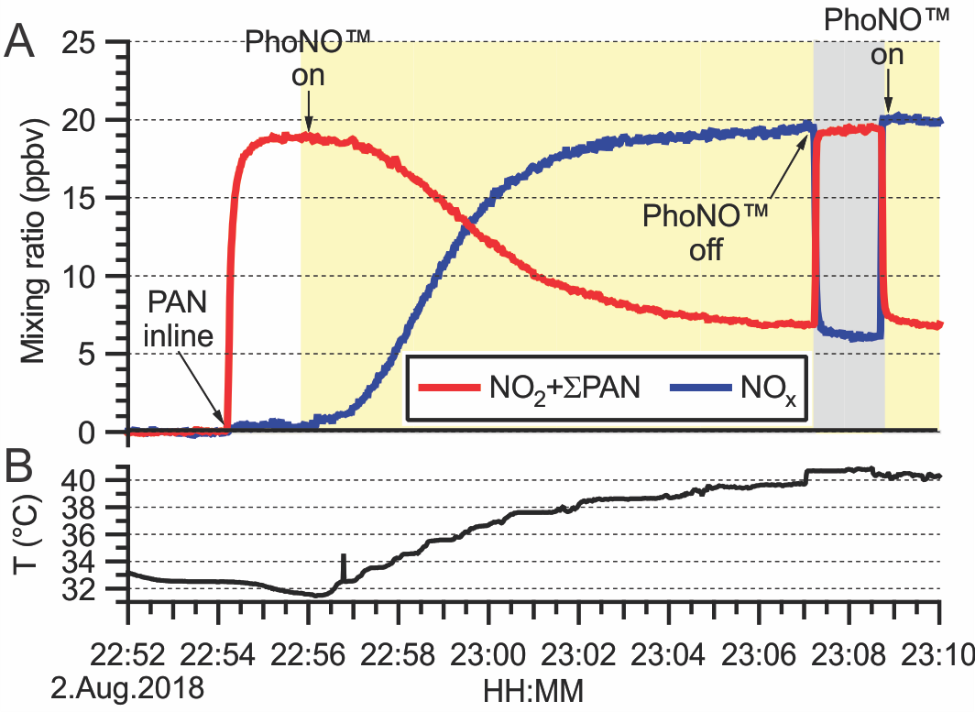


Figure S4. (a) Time series of NO2+ΣPAN (shown in red color) and of NOx (shown in blue color). (18.8±0.1) ppbv of PAN were added at 22:54. The converter was operated at a pressure of 417 Torr (3.3 sec residence time) and turned on at 22:56. Over time, more and more PAN dissociated to NO2, which photodissociated and was observed as NO in the NOx channel. When the converter was turned off at 23:07, (19.3±0.1) ppbv of NO2+ΣPAN and 6.2±0.2 NOx (NO2) were observed. The amount of NO2 was less during this time than before because the thermal dissociation of PAN is reversible; the NO generated by photolysis titrates the PA radical, speeding up the thermal dissociation. (b) Time series of temperature next to the photoreactor cell, measured using a K-type thermocouple inserted into the converter.

Shown in the bottom panel of Figure S4 is the corresponding time series of temperature, measured via a K-type thermocouple whose junction was located on the outside of the photolysis cell. The decrease in NO2+ΣPAN was accompanied by an increase in temperature, thermally dissociating higher amounts of PAN to NO2, which in turn photodissociated to NO and was observed in the NOx channel.

When the converter was turned off at 23:07, (19.3±0.1) ppbv of NO2+ΣPAN and (6.2±0.2) NOx (mostly NO2) were observed. From the extent of thermal dissociation (~31% dissociated at 23:08) and using a recent expression for TD of PAN, 2.8×1016 sec-1 × e(-113 kJ/mol)/(RT), [10](#_ENREF_10) and a residence time of 3.3 sec, we estimate that the internal temperature within the photolysis chamber in this particular experiment was 66 °C. However, this temperature is a lower estimate since the reverse of reaction (12) converts some NO2 back to PAN. The converter's LEDs are cooled using high-efficiency fans; these likely have transferred some of the heat to the surrounding tubing, such that the effective residence time was likely longer (and the temperature needed to achieve the effect lower).

When the converter's LEDs were turned back on at 23:09, the ratio of NO2+ΣPAN to NOx (=NO) was considerably lower (~66% dissociated), consistent with an internal temperature of 75 °C. The greater extent of dissociation is rationalized by photodissociation of NO2 to NO which in turn titrates the PA radical, driving equilibrium (12) towards the right, i.e., towards dissociation.

CH3C(O)O2 + NO CH3O2 + CO2 + NO2 (13)

CH3O2 + NO HCHO + HO2 + NO2 (14)

*Nitric acid*. Figure S5 shows a time series of an experiment in which the photo-conversion of HNO3 was investigated. A challenge with HNO3 was its slow equilibration with respect to partitioning to the inner walls of the Teflon™ tubing, manifesting itself with long equilibration times before stable mixing ratios were observed. An additional complication was that the permeation tube co-emitted some NO and NO2.

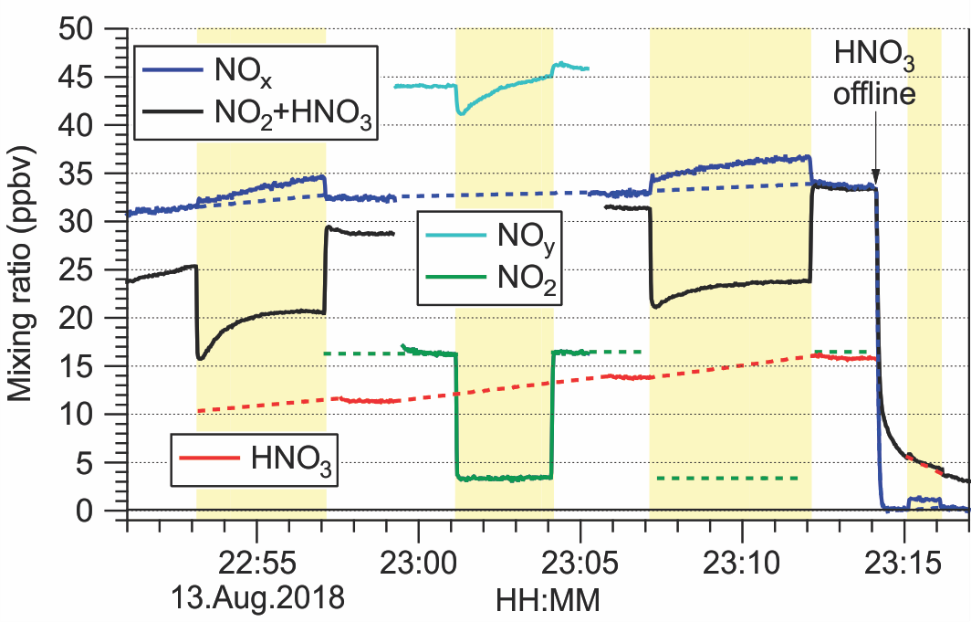


Figure S5. Time series of NO production from HNO3 photolysis at a cell pressure of 480 Torr. The solid lines indicate observed data, whereas the dashed lines indicate interpolated data.

In the experiment shown in Figure S5, the CRDS sampled the output of the Dynacalibrator from 22:43 onwards (the time series was truncated for clarity). One CRDS channel was operated in NOx mode (i.e., with O3), while the other sampled from a quartz inlet heated to 600 °C and quantified NO2+HNO3. From 22:59 to 23:06, the O3 addition point was switched, such that one channel quantified NO2 and the other NOy. Between 22:58 and 23:00, the following mixing ratios were observed: NOx = 32.6 ppbv, NO2 = 16.2 ppbv, and NOy = 44.1 ppbv. From this, we calculate NO = NOx - NO2 = 16.4 ppbv and NOz = NOy - NOx = 11.5 ppbv ≈ HNO3. The NO2+HNO3 channel measured 28.8 ppbv, which is greater than the sum of NO2 and NOz (27.7 ppbv); this difference is due to partial oxidation of NO in the quartz inlet heated to 600 °C.

When the converter's LEDs were turned on at 22:53 and again at 23:07, the mixing ratio in the NOx channel increased by up to 2.7 ppbv, indicating that a molecule other than NO2 photo-dissociated to NO. The response was not instantaneous. Rather, the NOx mixing ratio slowly increased during the irradiation. The NO2+HNO3 signal, while not quantitative, showed an initial sharp decrease in signal, which was followed by what seemed like a recovery period. The decrease in signal is mainly due to NO2 photolysis but was less (maximum of ~9 and ~10 ppbv) than the decrease observed in the pure NO2 channel at 23:02 (~15.4 ppbv). It is unclear if this shape is due to a process in the heated quartz inlet of the TD-CRDS or if it is the result of a process within the converter, or a combination thereof.

The NOy signal observed during the photolysis period from 23:01 to 23:04 showed an initial decrease and a recovery qualitatively similar to what was observed in the NO2+HNO3 channel. In contrast, the change in NO2 mixing ratio (by 12.9 ppbv), when the LEDs were switched on or off, was immediate and constant.

When the source was taken offline at 23:13, HNO3 was still observed as it outgassed from the inner walls of the Teflon™ tubing. Most of this HNO3 originated from the transfer tubing between the calibration gas addition point and the flow restriction (as this region has a larger surface area); it is therefore likely that this concentration was also flowing through the converter. No other components of NOy (e.g., NO, NO2, or HONO) would have been present during this time as they are all "better behaved" on Teflon™ tubing. At 23:15, the LEDs were turned on one more time, and an increase of 1.1 ppbv of NOx was observed. The ratio of produced NOx to gas-phase HNO3 was ~0.14 in this experiment.

The experiment was repeated the following day with higher HNO3 mixing ratios (up to 28 ppbv). When the converter's LEDs were turned on, NOx mixing ratios increased by up to 1.6 ppbv (ratio relative to HNO3 of ~0.06). This shows that the amount of NOx produced does not scale with the gas-phase HNO3 concentration entering the photolysis cell and suggests that the observed NOx was likely generated by a surface-driven process.

References

1. Mielke, L. H.; Osthoff, H. D., On quantitative measurements of peroxycarboxylic nitric anhydride mixing ratios by thermal dissociation chemical ionization mass spectrometry. *Int. J. Mass Spectrom.* **2012,** *310*, 1-9.

2. Ye, C. Z. Development of Purge-and-Trap Sample Preconcentrator for Enhanced Detection of Alkyl Nitrates by Thermal Dissociation Cavity Ring-Down Spectroscopy. University of Calgary, http://hdl.handle.net/11023/3510, 10.5072/PRISM/25688, Calgary, 2016.

3. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Troe, J., Evaluated Kinetic And Photochemical Data For Atmospheric Chemistry.3. Iupac Subcommittee On Gas Kinetic Data Evaluation For Atmospheric Chemistry. *J. Phys. Chem. Ref. Data* **1989,** *18* (2), 881-1097.

4. Burkholder, J. B.; Sander, S. P.; Abbatt, J. P. D.; Barker, J. R.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Orkin, V. L.; Wilmouth, D. M.; Wine, P. H., *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 18*. National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology: Pasadena, California, 2015.

5. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J., Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species. *Atmos. Chem. Phys.* **2004,** *4*, 1461-1738.

6. England, C.; Corcoran, W. H., The Rate and Mechanism of the Air Oxidation of Parts-per-Million Concentrations of Nitric Oxide in the Presence of Water Vapor. *Ind. Eng. Chem. Fundamen.* **1975,** *14* (1), 55-63.

7. Wild, R. J.; Edwards, P. M.; Dube, W. P.; Baumann, K.; Edgerton, E. S.; Quinn, P. K.; Roberts, J. M.; Rollins, A. W.; Veres, P. R.; Warneke, C.; Williams, E. J.; Yuan, B.; Brown, S. S., A Measurement of Total Reactive Nitrogen, NOy, together with NO2, NO, and O3 via Cavity Ring-down Spectroscopy. *Environm. Sci. Technol.* **2014,** *48* (16), 9609-9615.

8. Reed, C.; Evans, M. J.; Di Carlo, P.; Lee, J. D.; Carpenter, L. J., Interferences in photolytic NO2 measurements: explanation for an apparent missing oxidant? *Atmos. Chem. Phys.* **2016,** *16* (7), 4707-4724.

9. Paul, D.; Osthoff, H. D., Absolute Measurements of Total Peroxy Nitrate Mixing Ratios by Thermal Dissociation Blue Diode Laser Cavity Ring-Down Spectroscopy. *Anal. Chem.* **2010,** *82* (15), 6695-6703.

10. Kabir, M.; Jagiella, S.; Zabel, F., Thermal Stability of n-Acyl Peroxynitrates. *Internat. J. Chem. Kin.* **2014,** *46* (8), 462-469.