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Supplement of

Formation of reactive nitrogen oxides from urban grime photochemistry

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S1. Characterization of Experimental Chamber

Known amounts of NO_2 in N_2 were flowed through the sample illumination chamber and IBBCEAS cell in order to characterize the observed HONO for different experimental variables. The current set up facilitates an efficient NO_2 surface hydrolysis, forming HONO. Results are shown in Fig. S1 for both dark and light experiments as a function of RH. An input NO_2 concentration of 6.0 ppm, based on the reported value from the supplier (Linde), was further diluted with N_2 using needle valves and mass flow meters with uncertainties of ± 0.5 mL/min to a concentration of (4.76 ± 2.4) $x10^{12}$ molecules/cm^3. The figure displays the measured NO_2 and HONO concentrations detected by the IBBCEAS as a function of RH. The calculated total concentration measured from the sum of NO_2 and twice the HONO, following the mass balance implied by Equation 1, was (3.6 ± 0.3) $x10^{12}$ molecules/cm^3 which is within error of that calculated from the NO_2 concentration coming from the cylinder reported above. This suggests that this technique can quantify the total concentration of NO_2 + HONO here, though cannot accurately speciate NO_2 and HONO. Fig. S1b shows that the total concentration decreases upon illumination, due to the photolysis of NO_2 and HONO. The HONO concentration measured is independent of relative humidity within the 30% coefficient of variability measured between samples. No NO_2 was detected. This shows that the NO_2 to HONO conversion is complete within error, and that there is no significant impact on the IBBCEAS NO_2 + HONO response as a function of relative humidity. We note that if the photochemical product distribution between NO_2 and HONO changes with relative humidity, this will impact the total amount measured, because it takes two NO_2 molecules to make one HONO molecule. Thus a change from only NO_2 production to only HONO production would appear as a 50% change in the total amount detected as HONO. However, the changes measured as a function of RH are larger than can be explained by this mechanism.

Thus the total product concentrations from grime photochemistry may be safely compared as a function of RH. No values are shown below 13% in Fig. 3 and Fig. S1 because the RH meter is not sensitive below 10% and thus we cannot accurately report RH values. As well, when N_2 is flowed through the chamber without humidification, the total signal for NO_2 and HONO does not reach a plateau even after one hour. This indicates that the NO_2 is being irreversibly lost to the walls, likely forming complexes with the metal (Nishino and Finlayson-Pitts, 2012).

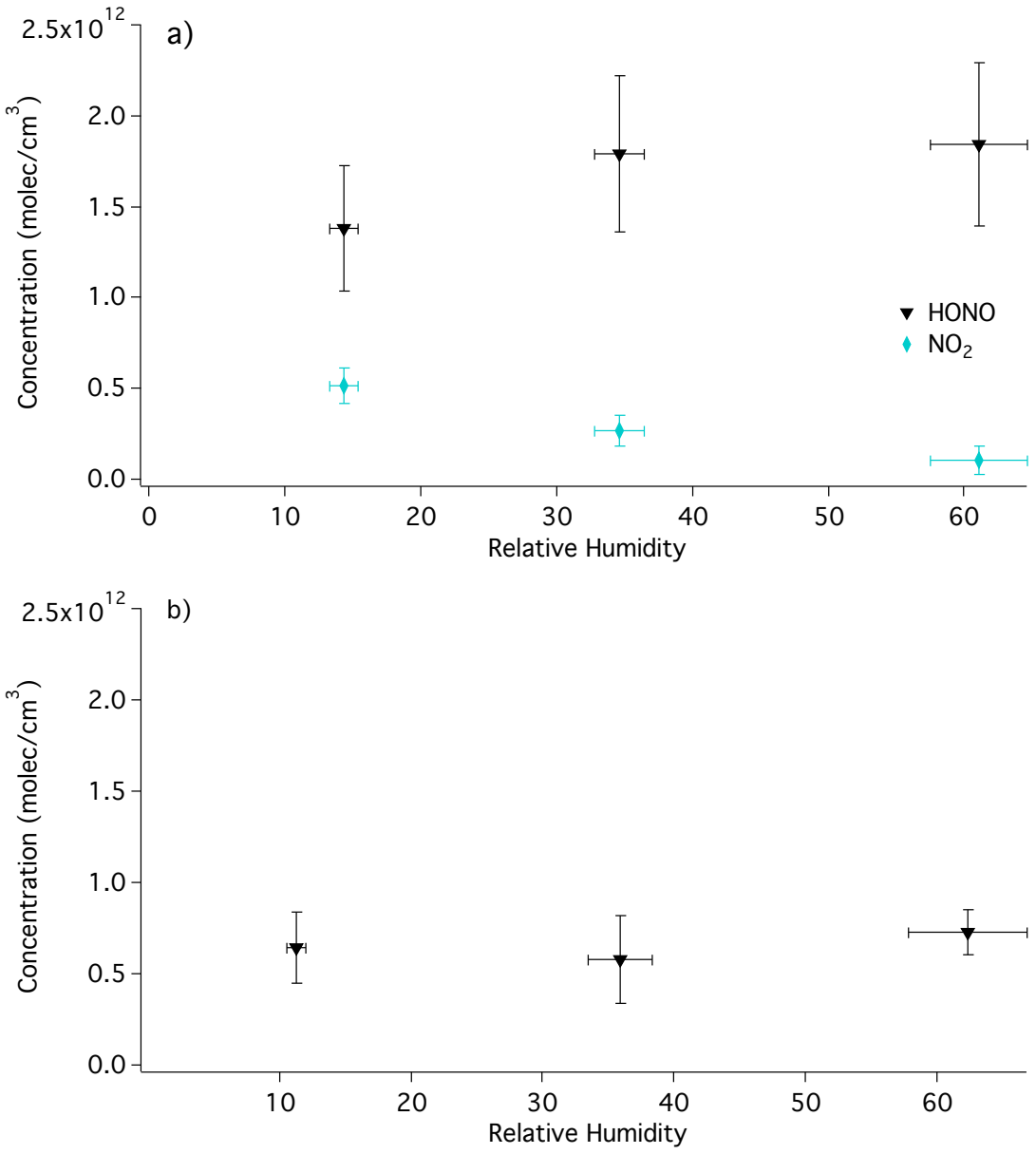

Figure S1: Concentrations of HONO and NO_2 for NO_2 flowed through the chamber and IBBCEAS cell as a function of RH a) in the dark and b) in the light. Only HONO concentrations are shown in Fig. S1b because no NO_2 was detected. The error bars represent one standard deviation of the average of three experiments.

Table S1: Inorganic ion content of grime used for photochemistry experiments (n=3)

	Chloride	Nitrate	Sulfate	Sodium	Potassium	Magnesium	Calcium
Concentration (μ g/cm^2)	4.8	0.73	4.27	4.9	0.34	1.27	2.11
Standard Deviation	0.1	0.01	0.04	0.2	0.01	0.05	0.05

References

Nishino, N. and Finlayson-Pitts, B. J.: Thermal and photochemical reactions of NO_2 on chromium(III) oxide surfaces at atmospheric pressure, Phys Chem Chem Phys, 14(45), 15840–15848, doi:10.1039/c2cp42292a, 2012.