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Photoenhanced Uptake of NO_2 and HONO Formation on Real Urban Grime

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Supporting Information

ABSTRACT: Nitrous acid (HONO) is one of the most important photochemical precursors of the hydroxyl radical in the sunlit urban atmosphere. The sources of HONO, however, are still poorly characterized, yet there is a disagreement between the field observations and the model results. Here, we show that light-induced NO_2 heterogeneous chemistry on authentic urban grime can make an important contribution to the total HONO levels in the urban atmosphere. The obtained results indicate that the effective uptake coefficients of NO_2 on urban grime in the presence of ultraviolet light [2.6×10^{15} photons cm^{-2} s^{-1} (300 nm < λ < 400 nm)] increased markedly from $(1.1 \pm 0.2) \times 10^{-6}$ at 0% relative humidity (RH) to $(5.8 \pm 0.7) \times 10^{-6}$ at 90% RH, exhibiting the following linear correlation with RH: $\gamma(NO_2) = (7.4 \pm 3.3) \times 10^{-7} + (5.5 \pm 0.6) \times 10^{-8} \times$ RH%. The flux densities of HONO mediated by light-induced heterogeneous conversion of NO_2 (46 ppb) on urban grime were enhanced by ∼1 order of magnitude from $(2.3 \pm 0.2) \times 10^9$ molecules cm^{-2} s^{-1} at 0% RH to $(1.5 \pm 0.01) \times 10^{10}$ molecules cm^{-2} s^{-1} at 90% RH. This study promotes light-induced NO_2 chemistry on urban grime being an important source of HONO and suggests that further experiments be performed in the future.

INTRODUCTION

Urban surfaces such as windows and walls are ubiquitous in dense urban environments. Thin organic films with thicknesses from 10 to 1000 nm, termed urban grime, that cover impervious surfaces in megacities have surface areas similar to that of atmospheric particulate matter (PM).[1−4] Hence, urban grime that consists of myriad organic compounds,[4−7] emitted in the urban atmosphere by vehicles, factories, and many other sources, could be considered as a separate environmental compartment. The presence of photochemically active organic compounds (e.g., PAHs)[6,8] on urban impervious surfaces could give rise to processes that have not been considered so far, affecting photochemistry in the atmospheric boundary layer. However, inorganic compounds Na_2SO_4, $NaNO_3$, and NaCl have also been found in urban grime, suggesting that urban grime is a mixture of organics and inorganics.[2,9]

Nitrous acid (HONO) is one of the key species in urban atmospheric chemistry as it has been shown that HONO photolysis makes an important contribution to the hydroxyl radical (OH) budget of the atmosphere.[10−13] It has been shown that photolysis of HONO can be responsible for ≤30% of OH formation during the day in the urban atmosphere.[13] Although several HONO sources were suggested in the literature, (i) the photosensitized reduction of nitrogen dioxide (NO_2) on soil,[14] (ii) the photolysis of adsorbed nitric acid (HNO_3) on ambient surfaces,[3,15,16] and (iii) bacterial production of nitrite in soil[17,18] and/or desorption of adsorbed HONO from soil surfaces during the day,[19,20] the observations show that HONO concentrations during the day are still higher than model outcomes and that the total contribution of HONO to the formation of OH was underestimated.[21] For example, three HONO sources (i.e., a light- and NO_2-dependent source, heterogeneous reaction of NO_2 with water layers in the dark, and direct HONO emissions) were coupled in the WRF-Chem model (Weather Research and Forecasting model coupled with Chemistry) to evaluate the impact of previously not considered HONO sources on the budgets of HONO and hydroxyl radicals in the coastal regions of China.[22] The outcomes from this model have shown that the additional HONO sources improved significantly the HONO and OH simulations during the day.[22] However, our current understanding is still in its infancy, and there is a discrepancy between the field observations and the results from photochemical models.[22,23] For example, an unknown HONO

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source strength of 165−600 ppt h^{-1} was reported as missing to explain the observed HONO levels based on known sources and sinks.[24] This is potentially significant, as HONO is the main primary OH source in the urban environment,[10−13] and any missing source in models[22,23] can lead to an underestimation of the oxidative capacity of the atmosphere.

Donaldson and co-workers[3] have shown that there is the potential for significant recycling of nitrogen oxides in the form of NO_2 and/or HONO upon photolysis of adsorbed HNO_3 into the atmosphere from urban grime.

In this study, we present experimental results demonstrating the enhanced formation of HONO upon light-induced heterogeneous reaction of NO_2 with authentic urban grime samples. The reactive uptakes of NO_2 and HONO formation were compared between the bare glass surface and glass covered with urban grime in the dark and under light irradiation at different relative humidities. Here we show that, depending on the relative humidity, large quantities of HONO are formed upon light-induced heterogeneous conversion of NO_2 on authentic urban grime.

EXPERIMENTAL PROCEDURES

Urban Grime. Urban grime was collected by placing several rectangular borosilicate glass plates (45 cm × 1.5 cm) outside on the roof of the building located in downtown Guangzhou. The glass plates were mounted on the frame (150 cm × 45 cm) and positioned vertically simulating a glass window. The plates were placed in the shade and protected from rain. The grime was collected during the "dry season" from November 1 to November 30, 2018. After a period of 4 weeks, the glass plates were carefully transported to the laboratory for further investigation.

Flow Tube Reactor. The flow tube reactor is operational under gas-phase laminar flow conditions (see the Supporting Information for details). The flow tube reactor used in this study was previously applied to assess the uptake coefficients of NO_2 on various indoor surfaces and respective HONO formation.[25−28]

NO_x and HONO Measurements. NO_2 mixing ratios were simultaneously measured by a chemiluminescence instrument (Eco Physics, model CLD 88p) and a photolytic (metal halide lamp) converter (Eco Physics, model PLC 860). The gas-phase HONO concentration was measured using a LOng Path Absorption Photometer (LOPAP, QUMA). Briefly, HONO is sampled in an aqueous solution in an external sampling unit. Then, after its chemical conversion into an azodye (550 nm), HONO is measured via long-path absorption in the visible wavelength range. The long-path absorption cell consists of Teflon tubing (Teflon AF2400). The Teflon tubing has a low refractive index that allows light to be transferred in total reflection. The detection limit of LOPAP was <30 ppt with a total accuracy of ±10% during all of the experiments. The actual time response was ∼2.5 min at gas flow and pump flow rates of 1 L min^{-1} and 500 μL min^{-1}, respectively.

RESULTS AND DISCUSSION

Reactive Uptake of NO_2. The effective uptake coefficient of NO_2 [$\gamma(NO_2)$] defines the reaction probability of gas-phase NO_2 with the deposited urban grime on the glass surface. The effective uptake coefficients of NO_2 were estimated as follows:

$$\gamma(NO_2) = \frac{4k_{NO_2}}{\overline{\nu}_{NO_2} A} \quad (1)$$

where k_{NO_2} is the pseudo-first-order rate constant for the reaction between NO_2 and urban grime on the glass plate, $\overline{\nu}_{NO_2}$ is the average molecular speed of NO_2, and A describes the geometry of the flow tube as a ratio between the glass surface (S) and the volume of the reactor (V).

Because we used a glass substrate, there will be no strong enlargement of the real glass window surface with grime on it. It might be different if urban grime forms on highly porous surfaces (soil and mineral dust),[29,30] but that is not the case here. For this reason, the effective uptake coefficient is more appropriate to apply in the model studies than the "true uptake coefficients" that can be obtained by measuring the "BET surface area" of highly porous surfaces.[31] The effective uptake coefficients of NO_2 on real urban grime as a function of the initial NO_2 mixing ratios under light irradiation (3.5×10^{16} photons cm^{-2} s^{-1} nm^{-1}) at 50% relative humidity (RH) shows irreversible dependence consistent with a Langmuir−Hinshelwood mechanism[32] (see the Supporting Information). The effective uptake coefficients of NO_2 on bare glass and a glass covered with an authentic urban grime were investigated as a function of different RHs at 296 K (Figure 1) in the dark and

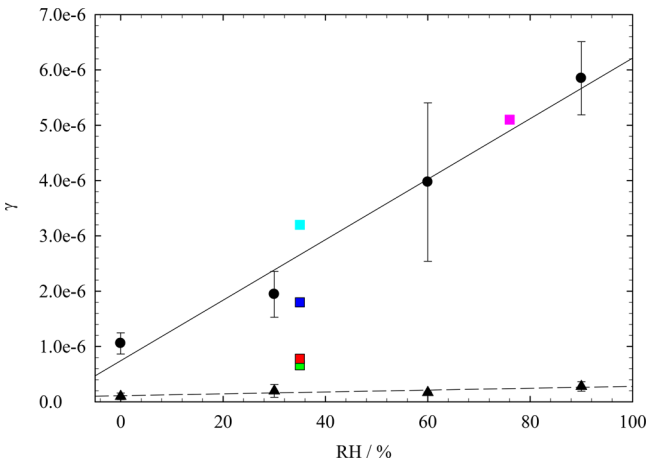

Figure 1. Effective uptake coefficients of NO_2 (▲) on bare glass, (●) on authentic urban grime as a function of the relative humidity, under UV light irradiation, at initial NO_2 mixing ratio of 46 ppb. The error bars are 1σ. (■, light blue) pyrene,[32] (■, pink) benzophenone/catechol,[33] (■, green) fluoranthene/KNO_3,[34] (■, red) phenanthrene/KNO_3,[34] and (■, dark blue) pyrene/KNO_3.[35]

under light irradiation. $\gamma(NO_2)$ values on bare glass under irradiation ranged between $(1.0 \pm 0.6) \times 10^{-7}$ at 0% RH and $(2.7 \pm 0.9) \times 10^{-7}$ at 90% RH. The $\gamma(NO_2)$ values on authentic urban grime in the presence of light (300 nm < λ < 400 nm) were 1 order of magnitude higher; i.e., $\gamma(NO_2) = (1.1 \pm 0.2) \times 10^{-6}$ at 0% RH, and $\gamma(NO_2) = (5.8 \pm 0.7) \times 10^{-6}$ at 90% RH. Figure 1 shows a very weak dependence of $\gamma(NO_2)$ on relative humidity on a bare glass surface under irradiation. On the other hand, a strong dependence of $\gamma(NO_2)$ on relative humidity on urban grime was observed in the presence of light (eq 2). The regression line represented in Figure 1 corresponds to

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$$\gamma(NO_2) = (7.4 \pm 3.3) \times 10^{-7} + (5.5 \pm 0.6) \times 10^{-8} \times \%RH \quad (2)$$

where $R^2 = 0.98$.

To the best of our knowledge, no other studies of the reaction between NO_2 and real urban grime as a function of RH are published in the literature to compare the results presented here. The reactive uptakes of NO_2 on urban grime under light irradiation increased 5-fold from $(1.1 \pm 0.2) \times 10^{-6}$ at 0% RH to $(5.8 \pm 0.7) \times 10^{-6}$ at 90% RH. The effective uptake of NO_2 at 90% RH is slightly higher than $\gamma(NO_2)$ on a mixture of a photosensitizer (benzophenone) and catechol (5.1×10^{-6}) at 76% RH.[33] $\gamma(NO_2)$ at 90% RH is almost 1 order of magnitude higher than $\gamma(NO_2)$ on artificial urban grime [for fluoranthene/KNO_3, $\gamma(NO_2) = 6.6 \times 10^{-7}$ at 35% RH; for phenanthrene/KNO_3, $\gamma(NO_2) = 7.8 \times 10^{-7}$ at 35% RH[34]] and 3 times higher than $\gamma(NO_2)$ on pyrene/KNO_3 [$\gamma(NO_2) = 1.8 \times 10^{-6}$ at 35% RH[35]] under similar irradiance conditions and initial NO_2 mixing ratios. The $\gamma(NO_2)$ values on artificial urban grime containing an inorganic compound (KNO_3) were 2−3 times lower than $\gamma(NO_2)$ values on a pure organic film consisting of either fluoranthene (1.07×10^{-6}), phenanthrene (1.34×10^{-6}), or pyrene (3.2×10^{-6}), indicating that the presence of nitrates reduces the effective uptake coefficients of NO_2.[34] Because the authentic urban grime contains a mixture of both organic and inorganic compounds,[4] a detailed study of their chemical composition could help to reveal the plausible reaction mechanism. The $\gamma(NO_2)$ values on bare glass under dark conditions were on the order of 10^{-8}, in good agreement with those from previous studies.[26,36,37]

Effect of Light on the Effective Uptake Coefficients of NO_2 and Production of HONO. A typical signal describing the uptake of NO_2 (46 ppb) on urban grime and formation of HONO is given in Figure 2. A clear HONO formation of 1.3 ppb is evident upon light-induced heterogeneous reaction of NO_2 with urban grime. Gaseous NO_2 was running for ∼24 h to obtain a stable signal. In position A, the injector is pushed to the end of the reactor and there is no contact between the NO_2 and urban grime. In position B, the injector is pulled back, allowing urban grime to be exposed to NO_2. The region from position B to C shows the formation of ∼0.5 ppb of HONO on urban grime under dark conditions. In position C, the injector is pushed again to the end of the flow tube reactor, and from position C to D, HONO goes back to zero. In position D, the injector is pulled back to allow contact between gas-phase NO_2 and urban grime under light irradiation. From position D to E, a stable formation of HONO of ∼1.3 ppb can be observed due to the effect of light on the reaction between NO_2 and urban grime. In position E, the light was switched off and the HONO mixing ratio decreases to the same level as in the dark.

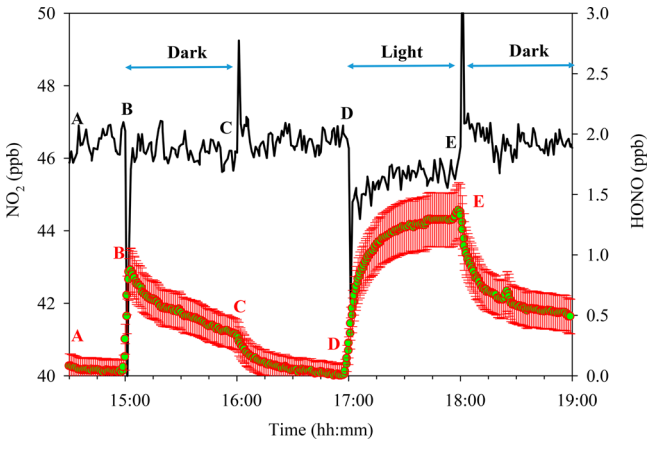

Figure 2. Typical signal of NO_2 uptake (black) and signal of build-up of HONO (green) under light irradiation of the urban grime. Positions A to E are explained in the core of the paper. NO_2 = 46 ppb, 60% RH, T = 293 K. Error bars correspond to 10% measurement uncertainties by LOPAP (red).

The same experimental procedure was applied to the bare borosilicate glass plate and then to the glass plate covered with urban grime to separate the contribution of 1-month-old urban grime versus clean glass to HONO production in the dark and under light irradiation.

HONO Flux Density. Figure 3 summarizes the results obtained as HONO formation rates for a unit of exposed surface area, hereafter the flux density of HONO (molecules per square centimeter per second), at a given initial NO_2 mixing ratio (46 ppb in this case).

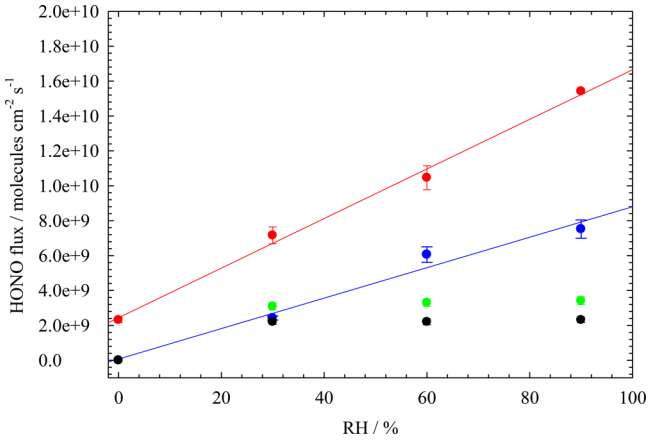

Figure 3. HONO flux densities as a function of relative humidity (●, black) on bare glass in the dark, (●, green) on bare glass under light irradiation, (●, blue) on urban grime in the dark, and (●, red) on urban grime under light irradiation. Error bars are 1σ. These HONO flux densities correspond to initial NO_2 mixing ratio of 46 ppb.

On bare borosilicate glass, the extent of HONO formation slightly increased with relative humidity, which can be described by the heterogeneous reaction of NO_2 on glass surfaces under dark conditions.[36] A slight increase in the extent of HONO formation was observed during the light irradiation of the bare glass as compared to the dark conditions. Similarly, nitrogen oxides, NO_2 and/or HONO, have been detected upon irradiation of urban grime.[3] The level of generation of NO_2 and/or HONO increased with relative humidity up to 35%, after which the production becomes independent of RH.[3] The photoenhanced HONO formation occurring on bare borosilicate glass has been previously reported.[26] The photo-enhanced HONO formation on clean borosilicate glass has been ascribed to photosensitized reactions of gas-phase NO_2 with the adsorbed traces of organic compounds on the glass that have not been removed by the cleaning procedure.[37] A recent study[16] demonstrated that HNO_3 photolysis cannot explain the significant HONO levels formed during the day in the atmosphere. In contrast to the previous studies,[15,38,39] a very low HNO_3 photolysis frequency for HONO formation of $J(HNO_3 \rightarrow HONO) = 2.4 \times 10^{-7}$ s^{-1} (0° SZA, 50% RH) was

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observed,[16] indicating that photolysis of HNO_3 is of minor importance with respect to daytime HONO formation in urban air.[40,41]

While authentic urban grime eliminates gas-phase NO_2 (Figure 2), it gives rise to gaseous HONO with a conversion yield of ~80%, like NO_2 to HONO conversion on the soil surface,[14] establishing the light-induced NO_2 to HONO conversion on urban grime as an important source of HONO in the urban environment. The flux densities of HONO in the dark and under light irradiation (see Figure 3) increased with RH. As one can see in Figure 3, there is significant HONO production under light irradiation on urban grime compared to the dark. Thus, adsorbed water on urban grime seems to be necessary for the formation of HONO. The presence of photosensitizers (e.g., anthraquinone, pyrene, and phenanthrene) on urban grime[33,35,42,43] could possibly explain photoenhanced HONO formation following the heterogeneous reaction of NO_2 with authentic urban grime. The increase in relative humidity could lead to a decreasing viscosity of urban grime so that the organic fraction may become accessible for reaction.[43]

The results from this study can be used to calculate the HONO source strength, giving production rates of 110 ppt h^{-1} during the "wet season" (90% RH) and 53 ppt h^{-1} during the "dry season" (30% RH), by assuming that a 20 m building height is covered by grime. Recently, a detailed model analysis of the HONO budget in London revealed a missing daytime source related to NO_2 and sunlight.[44] The effective uptake coefficients from this study can be integrated in such photochemical models to account for the unknown daytime HONO sources in an urban area. For example, a one-dimensional framework based on regional and three-dimensional chemical transport models (CTMs)[23] or The Weather Research and Forecasting/Chemistry (WRF-Chem) model[45] can consider the effective uptake coefficients from this study and account for the additional HONO formation in Guangzhou. Because HONO is an important source of OH in megacities,[10,11,46] the accurate quantification of HONO during the day is of paramount importance with regard to the OH concentrations and thus the oxidation capacity of the urban atmosphere.

Future studies should consider assessing the formation of HONO from urban grime collected in different cities under different conditions (season, temperature, and humidity).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.9b00308.

Information about materials and methods and description of the flow tube reactor, comparison of spectral irradiance $E(\lambda)$ emitted by ultraviolet−visible lamps and the outdoor solar spectral irradiance (Figure S1), effective uptake coefficients of NO_2 on real urban grime as a function of the initial NO_2 mixing ratios (Figure S2), and procedure for the estimation of HONO production in the flow tube reactor (PDF)

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Notes

The authors declare no competing financial interest.

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