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Article

Photoenhanced Heterogeneous Uptake of NO_2 and HONO Formation on Authentic Winter Time Urban Grime

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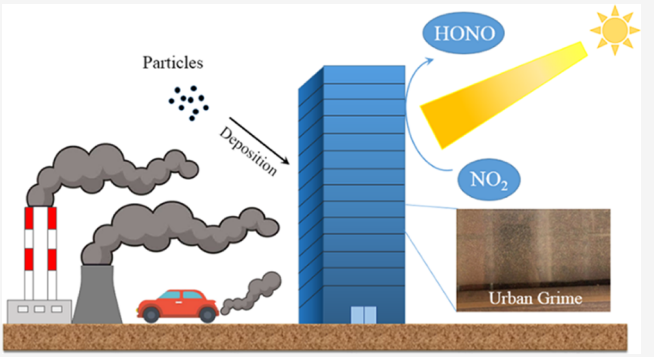
ABSTRACT: Heterogeneous reactions of NO_2 on surfaces seem to be an important sink for NO_2 and a source for HONO in the atmosphere. Although heterogeneous reactions of NO_2 have been extensively investigated in laboratory studies, kinetic data about this reaction on real ambient surfaces are limited. Therefore, in the present study, we investigated the heterogeneous reaction of NO_2 on urban grime, representative of surface film in urban areas, under various experimental conditions using a Teflon box system. The role that light played in these reactions was also explored. It was found that the uptake coefficient (γ) of NO_2 and HONO yield both were significantly enhanced under UV conditions, which was consistent with the literature results. The γ of NO_2 on urban grime increased linearly with the increasing light intensity, whereas the yield of HONO seemed to be independent of the light intensity. In addition to the intensity of light, heterogeneous reactions of NO_2 on urban grime were also significantly affected by the initial concentration of NO_2 and relative humidity. On the basis of the data measured, the flux of HONO production from photoenhanced NO_2 uptake on urban grime was calculated to be $(3.8-10.0) \times 10^9$ molecules cm^{-2} s^{-1}. This result suggests an important role of urban grime in the daytime NO_2-to-HONO conversion and could be helpful to explain unknown daytime HONO sources in polluted urban areas.



KEYWORDS: *heterogeneous reaction, nitrogen dioxide, urban grime, nitrous acid, uptake coefficient*

INTRODUCTION

Nitrous acid (HONO) is of great significance in atmospheric chemistry. It is well known as an important precursor of the OH radical, which plays a critical role in the oxidation capacity of the atmosphere.[1−4] The reaction of gaseous NO with OH radicals is the major daytime source of HONO, whereas the heterogeneous reaction of NO_2 on wet particles is recognized as the dominant pathway in the nighttime.[5−8] However, recent field studies observed the unexpected high concentration of HONO during daytime hours that cannot be explained by the well-accepted gas-phase oxidation pathways or direct vehicle emissions, suggesting the existence of unknown daytime sources of HONO.[9,10] Given the strong active photochemistry in the daytime, photolysis of HNO_3 and nitrate on the surfaces of particles, ground, or leaves was proposed to be the potential source.[11−14] Additionally, heterogeneous reactions of NO_2 on various surfaces (e.g., humic acid, polycyclic aromatic hydrocarbons (PAHs), mineral dust, and soot) under irradiation were also examined.[15−27] Compared to dark conditions, the reactivity of NO_2 was found to be significantly promoted under irradiation. The uptake coefficient (γ) of NO_2 measured in the presence of light is 1 or 2 orders of magnitude higher than that in the absence of light.[22,28,29] Since HONO is one of the important products during the reaction, the significant enhancement of HONO formation is also observed along with the uptake of NO_2. Therefore, in addition to nighttime, heterogeneous reactions of NO_2 may also be of great importance in daytime chemistry for HONO formation. However, it is found that previous studies on the photoreaction of NO_2 were mostly focused on pure chemicals or simple proxies instead of ambient surfaces. Impurity in particles could alter the behaviors of heterogeneous NO_2 uptake and HONO formation. Liu et al.[27] reported that the presence of Na_2SO_4 can significantly diminish the γ of NO_2 and HONO yield in the heterogeneous reaction of NO_2 with pure fluorene. The photoenhanced γ of NO_2 showed a linear positive relation with relative humidity (RH) on humic acid particles, but it increased at first and then decreased with increasing RH on the mixture of humic acid and benzophenone particles.[17,30] Therefore, it is essential to investigate the heterogeneous

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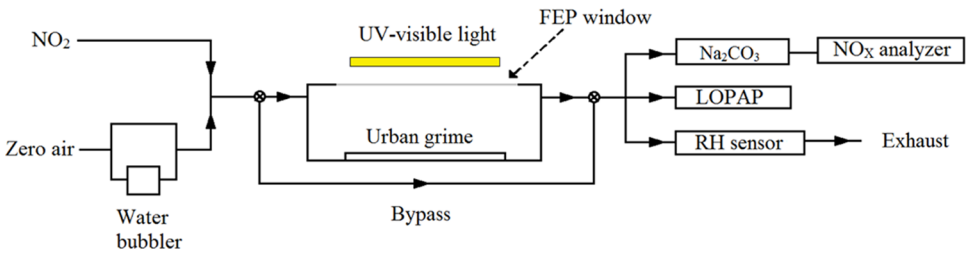

Figure 1. Schematic diagram of the Teflon box reactor system.

reaction of NO_2 on atmospheric relevant particles or surfaces; however, kinetic data about these reactions is scarce.

In urban areas, it is noted that urban surfaces (e.g., buildings, roadways, and sidewalks) can also provide a medium for the reactions of atmospheric trace gases similar to suspended particles. Via deposition and chemical processes, a film of a complex mixture of organic and inorganic materials, which is usually referred to as urban grime or environmental film, can also be formed on urban surfaces.[31−35] A model study revealed that the surface area provided by the ground surface was comparable to that of atmospheric particles,[36,37] suggesting the potential importance of the heterogeneous reaction of NO_2 on urban grime. A recent study has reported the photoenhanced uptake of NO_2 and HONO production on real urban grime, with γ of $(1.1-5.8) \times 10^{-6}$ at <1 to 90% RHs.[38] Our previous work has investigated the heterogeneous reaction of NO_2 on urban grime collected in Hong Kong, China, exploring effects of light and RH on γ of NO_2 as well as the yield of HONO formation.[29] However, it is noted that urban grime is a complex mixture of species, so different emission characteristics in different locations may alter the chemical compositions of urban grime.[31,32,39−45] Therefore, the heterogeneous behavior of NO_2 on more kinds of urban grime under different conditions should be investigated to better quantify the roles of these processes in HONO production and urban air quality.

Therefore, in this study, a series of experiments were further performed to investigate the heterogeneous reactions of NO_2 on urban grime, which was collected in north China during the heating season, using a Teflon box reactor. The photoenhanced heterogeneous uptake of NO_2 and HONO formation on urban grime were presented and the influence of experimental conditions (i.e., NO_2 concentration, light intensity, and RH) was explored. The results obtained are helpful in understanding the important role of urban grime in the daytime NO_2-to-HONO conversion.

EXPERIMENTAL SECTION

Apparatus. Experiments of heterogeneous reactions of NO_2 on urban grime were carried out in a flow reactor system. The schematic diagram of the reactor system is shown in Figure 1. The reactor consists of a Teflon box (inner size of 30 cm × 12 cm × 5 cm) with a 30 cm × 12 cm fluorinated ethylene propylene (FEP) window on the top. Urban grime samples were collected by placing 27 cm × 10 cm quartz glass plates on an open balcony on the second floor of a building in downtown Qingdao, Shandong Province (36.08°N, 120.39°E) during the heating season from December 10, 2020, to January 10, 2021. The weight of urban grime collected was ∼0.016 g. The heating season is a period of winter time (from November 15 to March 15 of the next year) in North China Plain for residential heating. Coal is the most common residential heating fuel in urban areas of China. More details about the experimental apparatus and sample preparation can be seen in our previous study.[29] Experiments were carried out at room temperature (∼295 K) and different RHs in the dark or under UV irradiation. UV−vis light (18 W, Arcadia Products Plc., U.K.) was used to generate light, and light intensity was controlled by the number of lamps. Spectral irradiance was measured by a Spectro-Radiometer (Specbos 1211UV, JETI Technische Instrumente GmbH, Germany), and the light spectrum is shown in Figure S1. The photolysis frequency of NO_2 was measured by a CCD spectrometer (PFS-100, Focused Photonics (Hangzhou) Inc., China) to assess the interference of NO_2 photolysis on these processes. RH was controlled by adjusting the relative flow rate of zero air (free of NO_x, O_3, SO_2, CO, and hydrocarbons), which was generated by a zero air supplier (Model 111, Thermo Fisher Scientific), passing through a water bubbler to the total airflow. The exact value of RH was also monitored by an RH probe (RH-USB, Omega). Prior to experiments, a quartz glass plate with urban grime was placed in the reactor. A gas flow containing NO_2 (10 ppmv standard gas, Qingdao Weierda Gas) was diluted with zero air before entering the reactor. The total 3 LPM gas flow was alternatively directed through either bypass or box reactor via valves. The NO_2 concentration in the total flow was ∼20 to 135 ppbv. The residence time of air in the box reactor was calculated to be 36 s. In blank experiments, a clean glass plate was placed in the reactor instead of the glass plate with urban grime to obtain blank results.

Detection of Reactants and Products. The NO_2 concentration was measured by a chemiluminescence analyzer with a molybdenum converter (Model 42i, Thermo Fisher Scientific) coupled to a sodium carbonate denuder (60 cm × 1 cm id Teflon tube). The sodium carbonate denuder was used to remove HONO in the gas phase, which could lead to an overestimation in the measurement of NO_2 by an analyzer. The HONO concentration was measured by a long-path absorption photometer (LOPAP-03, QUMA, Germany) that has been applied in several studies.[46−50] The detailed description can be found in Heland et al.[51] Briefly, it is based on wet chemical sampling and photometric detection. HONO is absorbed by sulphanilamide−hydrochloric acid solution in a sampling unit. And then, the resulting solution is mixed with naphtylethylendiamine−dihydrochloride solution and subsequently converted to an azo dye. The azo dye is pumped into a detection unit consisting of a long tube, and the absorption spectra are measured to calculate the HONO concentration.

Amounts of metal in urban grime were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700, Agilent Technologies Inc.). Urban grime was scraped off from the sample plate and subsequently predigested in 7 mL of aqua regia and 1 mL of H_2O_2 (298 K) for 30 min. And then, the suspension was digested by

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ACS Earth Space Chem. 2022, 6, 1960−1968

microwave digestion at 120 °C for 60 min, 180 °C for 60 min, and 220 °C for 60 min. After that, the resulting solution was injected into ICP-MS to measure the concentrations of 10 metal elements (Al, Ca, Cu, Fe, Mg, Mn, Pb, Ti, V, and Zn).

In addition to metal elements, concentrations of polycyclic aromatic hydrocarbons (PAHs) in urban grime were also measured. Urban grime was scraped off from the sample plate and then extracted for 30 min sonication twice using 5 mL of acetonitrile saturated with the n-hexane solution. The extract was filtered and the resulting solution containing PAHs was analyzed by a gas chromatograph equipped with a mass spectrometer (GC−MS, TRACE 1300-ISQ LT, Thermo Fisher Scientific). The carrier gas was high-purity helium with a flow velocity of 0.7 mL min^{-1}. The column temperature was held at 80 °C for 2 min, heated to 180 °C for 5 min at a rate of 10 °C min^{-1}, and then heated to 300 °C for 5 min at a rate of 5 °C min^{-1}.

Determination of the Uptake Coefficient and the Yield. In this study, the uptake of NO_2 on urban grime was assumed to be a pseudo-first-order reaction, thus rate constant (k) of this reaction can be expressed by eq E1

$$k = \ln\left(\frac{[NO_2]_0}{[NO_2]_t}\right)/t \quad \text{(E1)}$$

where $[NO_2]_0$ is the initial concentration of NO_2, ppbv; $[NO_2]_t$ is the NO_2 concentration measured at the exit of the reactor, ppbv; and t is the resident time of NO_2 in the reactor, s. On the basis of the pseudo-first-order reaction assumption, the uptake coefficient (γ) of NO_2 can be calculated using eq E2

$$\gamma = \frac{4(k_p - k_b)}{\omega(S/V)} \quad \text{(E2)}$$

where k_p and k_b are the rate constants of NO_2 on urban grime or on clean glass (blank experiment), s^{-1}; respectively; ω is the mean molecular velocity, m s^{-1}; V is the volume of the reactor, m^3; and S is the surface area of the quartz glass plate, m^2. Accordingly, all γ calculated in this study represent the geometric uptake coefficient of NO_2.

Additionally, the yield and flux of HONO during the processes were also estimated. The yield of HONO production (Y_{HONO}), defined as the ratio of the net concentration of the formed HONO to the net concentration of the consumed NO_2 (eq E3), was also calculated.

$$Y^{HONO} = \frac{[\Delta HONO]_p - [\Delta HONO]_b}{[\Delta NO_2]_p - [\Delta NO_2]_b} \quad \text{(E3)}$$

where $[\Delta HONO]_p$ and $[\Delta NO_2]_p$ are concentrations of HONO generated and NO_2 consumed from NO_2 uptake on urban grime, respectively, ppbv; $[\Delta HONO]_b$ and $[\Delta NO_2]_b$ are concentrations of HONO generated and NO_2 consumed from NO_2 uptake on the clean glass plate, ppbv.

The flux of HONO production from urban grime was calculated by eq E4

$$\text{flux} = \frac{([\Delta HONO]_p - [\Delta HONO]_b)fP}{RATS} \quad \text{(E4)}$$

where f is the total flow rate of the reagent gas, m^3 s^{-1}; P is the ambient pressure, Pa; R is the gas constant, J mol^{-1} K^{-1}; T is the ambient temperature, K; A is Avogadro's constant; and S is the surface area of the quartz glass plate, m^2.

RESULTS AND DISCUSSION

Photoenhanced NO_2 Uptake and HONO Formation. Each experiment was conducted with the following experimental procedures as shown in Figure 2. First, the air was switched to bypass to measure the initial NO_2 concentration (step 1). When the initial NO_2 concentration was stable, the flow was switched back to pass through the box reactor to react with urban grime in the dark for ∼60 min (step 2). It was noted that HONO was the potential product formed during the reaction, thus, in addition to NO_2, the concentration of HONO was also monitored at the exit of the box reactor. And then, the lamp was turned on to investigate the effects of irradiation on the heterogeneous reactions of NO_2 with urban grime (step 3). After the reaction, the lamp was turned off and NO_2 was bypassed from the reactor to measure the concentration again (step 4). Figure 2 displays how the NO_2 and HONO concentrations changed during these processes when the sample was exposed to NO_2 in the dark or under irradiation. In some experiments, a clean glass plate was placed in the reactor to run the same procedures to obtain the blank results (Figure S2).

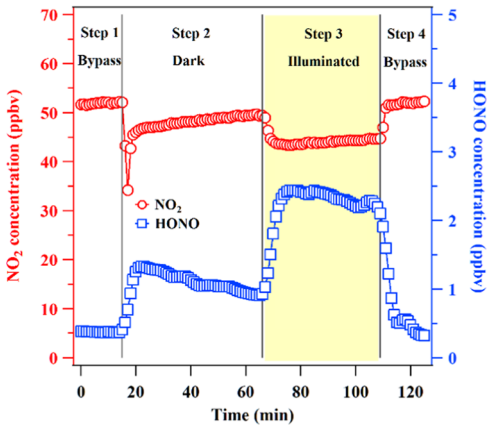

Figure 2. Temporal changes of NO_2 and HONO concentration during the NO_2 uptake experiment. Experimental conditions: UV−vis light irradiation of 5.2 W m^{-2}, initial NO_2 concentration of 52.2 ppbv, and RH of 64%. Red circles and blue squares represent the concentration of NO_2 and HONO, respectively.

As shown in Figure 2, in the absence of light, when NO_2 was just introduced into the reactor, its concentration rapidly decreased within 3 min first and then gradually increased until a steady-state condition was achieved (step 2). The steady γ value of NO_2 was calculated as $(0.51 \pm 0.12) \times 10^{-6}$. This value is higher than that reported in our previous study, which also determined the γ value of NO_2 on urban grime collected in Hong Kong, China, under dark conditions.[29] Because the same measurement method was employed, this discrepancy may be partly attributed to the different components of urban grime collected at different sites. Several studies have reported that the chemical composition of urban grime varies at different times or in different locations.[31,32,39,45] In this study, the sample was collected during the heating season. The higher γ value indicates that urban grime collected in Qingdao during the heating season could be more reactive to NO_2 compared to urban grime collected in Hong Kong, China. When the lamp was turned on, it was found that the NO_2 concentration started to decrease again (step 3), from ∼49 to ∼43 ppbv. Analogously, we also calculated the γ value after the NO_2

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ACS Earth Space Chem. 2022, 6, 1960−1968

concentration approached a plateau under irradiation. This value [$(1.52 \pm 0.04) \times 10^{-6}$] is 3 times larger than that under dark conditions, suggesting the significant role that light plays in the heterogeneous reaction of NO_2 on urban grime.

Figure 2 also shows the decrease in the NO_2 concentration with the concomitant formation of HONO. The yield of HONO formation was calculated as 24% in the absence of light. The possible mechanism for HONO formation is elucidated via NO_2 hydrolysis as shown in reaction R1.[7]

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \quad (R1)$$

Under irradiation, it is noted that HONO yield is also enhanced similar to the γ value. The increment of HONO yield suggests that there exist additional pathways for HONO formation. The photoenhanced NO_2 uptake and HONO yield have also been observed on other kinds of surfaces, such as Fe_2O_3, TiO_2, and polycyclic aromatic hydrocarbons (PAHs).[19−21,27,52−54] TiO_2 is well known as a photosensitizer.[55,56] When TiO_2 is excited by light, an electron in the conduction band and a hole in the valence band can be formed (R2). The electron can react with adsorbed NO_2 to form NO_2^-, facilitating the conversion of NO_2 and thereby promoting the uptake of NO_2 (R4). The formed NO_2^- subsequently combined with H^+, resulting in the formation of HONO (R5).

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (R2)$$

$$H_2O + h^+ \rightarrow H^+ + OH^\bullet \quad (R3)$$

$$NO_2 + e^- \rightarrow NO_2^- \quad (R4)$$

$$NO_2^- + H^+ \rightleftharpoons HONO \quad (R5)$$

Fe_2O_3 is also a ubiquitous photosensitizer. Heterogeneous uptake of NO_2 on α-Fe_2O_3 shows an enhancement under UV irradiation as well, yielding reduced nitrogen species on the surface of α-Fe_2O_3.[54]

Analogous to TiO_2 and Fe_2O_3, the enhancement of the NO_2 uptake on PAH particles under irradiation is also attributed to the promotion of NO_2 conversion on the surface; however, the detailed mechanism is different.[19−21,27] PAHs can get excited by irradiation, and then the electronically excited state of PAHs combines with NO_2 to form a [PAH^+-NO_2^-] complex via the electron transfer pathway. The complex then decomposes into PAH^+ and NO_2^- (R8). HONO is produced through the combination of NO_2^- and H^+.

$$PAH \xrightarrow{h\nu} [PAH]^* \quad (R6)$$

$$[PAH]^* + NO_2 \rightarrow [PAH^+ - NO_2^-] \quad (R7)$$

$$[PAH^+ - NO_2^-] \rightarrow PAH^+ + NO_2^- \quad (R8)$$

$$NO_2^- + H^+ \rightleftharpoons HONO \quad (R9)$$

During the heating season, large amounts of metals including Fe and Ti[57−60] as well as organics including PAHs[61−64] can be emitted along with the particulate matter. Table S1 lists concentrations of different metal elements in urban grime. The concentration of Fe and Ti in urban grime was measured as 31.38 ± 5.17 and 0.53 ± 0.07 mg g^{-1}, respectively. In addition to metal elements, concentrations of PAHs in urban grime were also measured as shown in Table S2. 16 PAHs were detected in urban grime with a total concentration of 4.04 ± 0.28 μg g^{-1}. Therefore, the significant increase in the γ value and HONO yield under irradiation observed in this study can be partially ascribed to the presence of TiO_2, iron oxides, or PAH components in the collected urban grime. However, it is noted that the concentration of Fe and Ti is at least 2 orders of magnitude higher than that of PAHs, thus it seems that the enhancement of NO_2 uptake as well as HONO yield under irradiation is mainly contributed by metal oxides rather than PAHs. Additionally, in consideration of the complexity of the composition of urban grime, the presence of other potential pathways responsible for HONO formation cannot be excluded. Further investigation on the products of NO_2 uptake on urban grime is warranted for a comprehensive understanding of the reaction mechanism.

Influence of Experimental Conditions. As mentioned above, the uptake of NO_2 by urban grime can be significantly enhanced in the presence of light. Thus, the effects of light intensity on this process were examined. Figure 3 shows a linear increase in γ with the increasing light intensity. The dependence of photoenhanced γ on light intensity can be described using eq E5

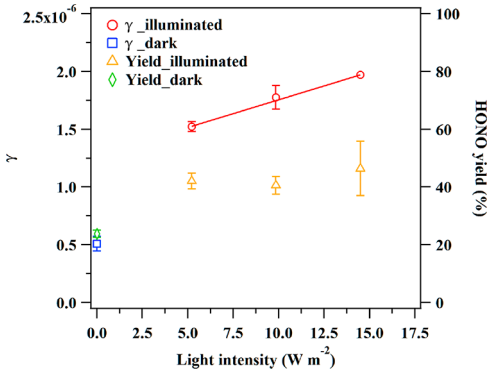

Figure 3. Uptake coefficients of NO_2 and HONO yield on urban grime as a function of the light intensity, at an initial NO_2 concentration of 52.2 ppbv and RH of 64%. The red circles, blue squares, yellow triangles, green diamond symbols, and error bars represent the average values of γ under UV−vis light and dark conditions and the average values of HONO yield under UV−vis light and dark conditions, and standard deviation, respectively.

$$\gamma = (4.8 \pm 0.4) \times 10^{-8} \times [\text{light intensity}](\text{W m}^{-2}) + (1.3 \pm 0.1) \times 10^{-6} \quad (E5)$$

To the best of our knowledge, no study has investigated the influence of light intensity on NO_2 uptake on authentic urban grime. Nevertheless, a similar linear dependence on light intensity has been found in PAHs,[19−21,27] humic acid,[17] humic acid + benzophenone,[30] and soot particles.[26] For example, Han et al.[17] reported that γ ranged from $(1.67 \pm 0.14) \times 10^{-6}$ under 68.5 W m^{-2} to $(4.37 \pm 0.45) \times 10^{-6}$ under 195 W m^{-2} on humic acid particles at 30 ppbv NO_2 and 22% RH. Although the γ value increases with the increasing light intensity, it seems that HONO yield is independent of light intensity (Figure 3). This observation is also consistent with the result of a previous study that investigated the influence of light intensity on the yield of HONO produced from the heterogeneous reaction of NO_2 on humic acid.[17] However, the HONO yield measured in the present study is much lower than that in their study (74%). This value is 1.7 times higher

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ACS Earth Space Chem. 2022, 6, 1960−1968

than the HONO yield measured in our study (43%). It is noted that nonvolatile products, such as nitrate and nitrite, can also be formed in the heterogeneous reactions of NO_2 with particles in addition to HONO. The discrepancy in the HONO yield between urban grime and humic acid suggests that urban grime may be prone to form nonvolatile products.

In addition to light intensity, we also investigated the effects of NO_2 concentration on the uptake of NO_2 and HONO formation. Figure 4 displays the change of γ and HONO yield

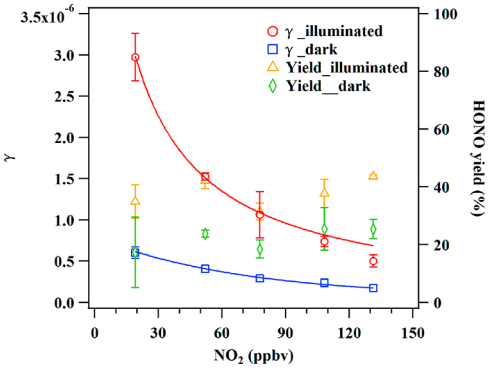

Figure 4. Uptake coefficients of NO_2 and HONO yields on urban grime as a function of NO_2 concentration, under UV−vis light irradiation of 5.2 W m^{-2} and at 64% RH. The red circles, blue squares, yellow triangles, and green diamond symbols and error bars represent the average values of γ under UV−vis light and dark conditions, the average values of HONO yield under UV−vis light and dark conditions, and standard deviation, respectively.

as a function of NO_2 concentration in the absence and presence of light. When the NO_2 concentration increased from 19 ppbv to 131 ppbv, γ decreased from $(0.60 \pm 0.07) \times 10^{-6}$ to $(0.17 \pm 0.02) \times 10^{-6}$ in the dark and decreased from $(2.97 \pm 0.29) \times 10^{-6}$ to $(0.50 \pm 0.07) \times 10^{-6}$ under irradiation. These results suggest that the uptake of NO_2 on urban grime is less efficient at higher NO_2 concentrations both under irradiation and dark. The dependence of photoenhanced γ on the initial NO_2 concentration under irradiation can be empirically described using eq E6

$$\gamma = \frac{1}{(9.9 \pm 1.3) \times 10^3 \times [NO_2](\text{ppbv}) + (1.4 \pm 0.3) \times 10^5} \quad \text{(E6)}$$

Previous studies also proposed that the increase in NO_2 concentration can significantly inhibit the uptake of NO_2 on various kinds of particles (e.g., PAHs, humic acid, mineral dust, and soot).[17,19−22,24,26,27] The Langmuir−Hinshelwood mechanism is usually used to explain such an inverse dependence.[19,21,22,27,30] NO_2 is first adsorbed on the surface of urban grime through gas-particle phase partitioning and then proceeds in the reactions with reactive species. Thus, the inverse dependence was attributed to the saturation of available adsorption sites. Although NO_2 uptake is negatively dependent on the initial NO_2 concentration, it is expected that HONO yield was rarely influenced by NO_2 concentration, which is consistent with the observation of previous studies.[17,19−21,30]

The influences of RH on NO_2 uptake on urban grime under dark and UV conditions are shown in Figure 5. The uptake of NO_2 on urban grime is significantly enhanced at higher RH both under dark and UV conditions compared to lower RH.

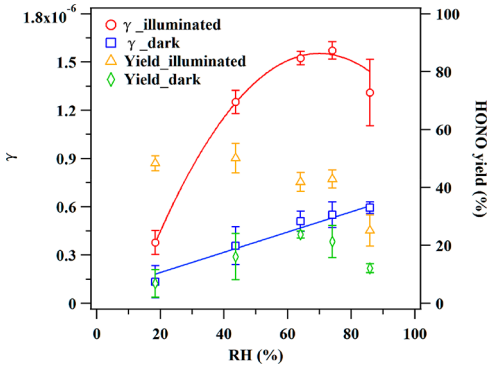

Figure 5. Uptake coefficients of NO_2 and HONO yields on urban grime as a function of RH under UV−vis light irradiation of 5.2 W m^{-2} and at an initial NO_2 concentration of 52.2 ppbv. The red circles, blue squares, yellow triangles, green diamond symbols, and error bars represent the average values of γ under UV−vis light and dark conditions, the average values of HONO yield under UV−vis light and in dark conditions, and standard deviation, respectively.

However, the trend of γ value for RH dependence is different between these experimental conditions. In the dark, γ linearly increase with the increasing RH. This may be ascribed to the hydrolysis of NO_2 on wet surfaces.[7] Similar trend has also been found for urban grime collected in Hong Kong, China.[29] It is noted that there exists an inflection point under irradiation. γ also increases from $(0.38 \pm 0.07) \times 10^{-6}$ at 18% RH to $(1.57 \pm 0.05) \times 10^{-6}$ at 74% RH at first, but then dropped to $(1.31 \pm 0.21) \times 10^{-6}$ at 86% RH. The dependence of photoenhanced γ on RH under irradiation can be empirically described using eq E7

$$\gamma = -(4.4 \pm 0.9) \times 10^{-10} \times ([RH](\%))^2 + (6.2 \pm 0.8) \times 10^{-8} \times [RH](\%) - (6.1 \pm 1.8) \times 10^{-7} \quad \text{(E7)}$$

As mentioned above, the chemical conversion of NO_2 on urban grime may mainly occur via three pathways under irradiation: (1) reacting with surface active sites, (2) reacting with the photoinduced oxidants (e.g., electron and trigger excited radicals), or (3) reacting with surface adsorbed water (i.e., hydration). Adsorbed water can occupy surface active sites and consequently inhibit the photoreaction of surface species, but it can also accelerate NO_2 hydration. Moreover, it is noted that adsorbed water can decompose into two OH radicals under irradiation, providing the additional pathway for NO_2 conversion.[24,52] Therefore, the increase in γ with the increasing RH requires that the role of adsorbed water in the promotion of NO_2 uptake prevails over its inhibition effects. Previous studies observed that the amount of water vapor uptake onto urban grime has a positive relation with RH (0−75%),[13,43] indicating that more water is accumulated on urban grime at higher RH. Consequently, the amount of adsorbed water or the hygroscopicity of urban grime significantly affects the trend of NO_2 uptake dependent on RH. This is also the possible explanation for the different inflection points observed on various kinds of particles (e.g., TiO_2, Arizona Test Dust, humic acid, and humic acid mixed with benzophenone).[24,28,52] For example, inflection point occurred at 15% RH on TiO_2 particles,[52] but occurred at 22% RH on humic acid mixed with benzophenone.[28] Moreover, a linear dependence of γ on RH was found on urban grime collected in south China under UV light.[38] This discrepancy may also be the result of the different

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ACS Earth Space Chem. 2022, 6, 1960−1968

composition, particle size, and hygroscopicity properties of urban grimes.

The change in the HONO yield as a function of RH is also investigated. Figure 5 shows that there exists an inflection point at ∼62% RH for HONO yield in the dark. The presence of water can promote the hydrolysis of NO_2 as shown in R1, resulting in higher HONO production. Furthermore, the adsorbed H_2O can also contribute to the H^+ transfer to generate HONO from nitrites formed on the surface.[18] However, with the increase in RH, the adsorbed H_2O can also compete with NO_2 for the surface active sites, resulting in a decrease in HONO yield along with γ. Baergen and Donaldson investigated the direct photolysis of urban grime and found that HONO formation increased as the RH increased to 35%, then plateaued, and even slightly decreased with further increase in RH.[13] This indicates that urban grime might be deliquescent and form water film at high RH, thereby preventing the release of HONO. This may be also the possible explanation for the observation of the decrease in the HONO yield at a higher RH. The HONO yield was reported as 28% at 5% RH and 46% at 70% RH on urban grime collected in Hong Kong, China under irradiation.[29] The yield in this study is in good agreement with that at ∼70% RH but higher than that at low RH. This discrepancy can be attributed to the differences in the chemical composition and hygroscopicity property in urban grime in Qingdao or Hong Kong, China.

■ ATMOSPHERIC IMPLICATION AND CONCLUSIONS

In this study, we investigated the heterogeneous reaction of NO_2 on urban grime collected in north China during the heating season. Under irradiation, NO_2 shows a much stronger reactivity to urban grime compared to dark conditions, resulting in higher HONO generation. The photoenhanced HONO formation via NO_2 uptake could further influence the oxidation capacity of the urban atmosphere given that it serves as the important reservoir for OH radicals.[1−4,65] On the basis of data collected, the flux of HONO was estimated using eq E4. Table 1 summarizes the results of HONO flux calculated at different experimental conditions, ranging from 3.8×10^9 to 10.0×10^9 molecules cm^{-2} s^{-1}. The daytime missing sources of HONO have been found in north China in several studies.[66,67] Spataro et al.[67] reported an average daytime missing source of 2.58 ppbv h^{-1} for the HONO formation rate in Beijing. Tang et al.[66] reported that this value could be up to 2.5 ppbv h^{-1} in the north China plain (Beijing−Tianjin−Heibei region). To calculate the HONO source strength from urban grime in urban areas, the urban surface−volume ratio (S/V) should be obtained. Typically, the S/V value was set as 0.1−0.3 m^{-1} in previous model studies.[68−70] Here, a middle value of 0.2 m^{-1} was used, and the formation rate of HONO contributed by urban grime was accordingly estimated to be 1.1−2.7 ppbv h^{-1} in the atmosphere. The calculated result was comparable to the reported missing source in north China, indicating that NO_2 uptake on urban grime could be an important pathway for daytime HONO formation in urban areas and should be considered in current atmospheric chemical models. Moreover, our results showed that the photoenhanced HONO production on urban grime collected in Qingdao ($3.8−10.0 \times 10^9$ molecules cm^{-2} s^{-1}) was 2 times larger than that of urban grime collected in Hong Kong, China ($1.9−5.3 \times 10^9$ molecules cm^{-2} s^{-1}).[29] Further investigation is still needed to study the reactivity of NO_2 on urban grime collected from different locations to better quantify the contribution of such heterogeneous reaction to the HONO source strength.

Table 1. Flux of HONO Production on Urban Grime at Different Scenarios

experimental conditions			
NO_2 (ppbv)	RH (%)	light intensity (W m^{-2})	flux of HONO production (molecules cm^{-2} s^{-1})
52.2	86	5.2	$(4.2 \pm 0.3) \times 10^9$
52.2	74	5.2	$(8.7 \pm 0.9) \times 10^9$
52.2	64	5.2	$(8.1 \pm 0.4) \times 10^9$
52.2	44	5.2	$(8.8 \pm 0.8) \times 10^9$
52.2	18	5.2	$(3.8 \pm 1.2) \times 10^9$
52.2	64	9.8	$(7.6 \pm 0.7) \times 10^9$
52.2	64	14.5	$(10.0 \pm 1.5) \times 10^9$
19.2	64	5.2	$(4.8 \pm 0.4) \times 10^9$
77.9	64	5.2	$(6.3 \pm 0.1) \times 10^9$
108.4	64	5.2	$(7.6 \pm 1.4) \times 10^9$
131.4	64	5.2	$(7.0 \pm 1.1) \times 10^9$

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00054.

Concentration of metal elements; concentration of PAHs; spectral irradiance of the UV−vis light; and results of blank experiments (PDF)

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Notes

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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on June 24, 2022, where the unit of S/V was used as "/dm" during the calculation of uptake coefficient throughout the paper. This error was corrected, and the updated version was reposted on July 23, 2022.

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