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Temperature dependencies of the degradation of NO, NO₂ and HONO on a photocatalytic dispersion paint†

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The photocatalytic decomposition of nitrogen oxides (NO_x) has attracted significant interest as a potential measure of reducing NO_x levels in the urban atmosphere. Since photocatalytic activity is highly variable depending on atmospheric conditions, the uptake of NO, NO_2 and HONO was studied on a commercial photocatalytic dispersion paint in a flow photoreactor as a function of the relative humidity and temperature. Since the relative humidity is a function of the surface's temperature, here both dependencies were carefully decoupled for the first time. In addition, for the first time the temperature dependence of the whole NO_x reaction system including the important intermediate HONO was investigated. While for NO and NO_2 strong negative humidity dependencies were observed, the photocatalytic uptake of HONO increased with humidity. For constant relative humidity no temperature dependence of the photocatalytic oxidation of NO was observed, whereas the photocatalytic NO_2 uptake decreased with increasing temperature, which is explained by a temperature dependent adsorption equilibrium of the surface active NO_2. HONO uptake showed a positive temperature dependence confirming the proposed photocatalysis of nitrite in a layer of adsorbed water on the surface of the photocatalyst. The missing/negative temperature dependencies of the photocatalysis of NO/NO_2 are overcompensated by their strong negative relative humidity dependencies, leading to increasing uptake for both pollutants when photocatalytic surfaces are heated by solar irradiation in the atmosphere.

1 Introduction

Nitrogen oxides (NO_x = NO + NO_2) are important trace species in the atmosphere. NO_x control photochemical ozone (O_3) formation and the oxidation capacity of the atmosphere, and lead to the acidification of the environment *via* their final oxidation product nitric acid (HNO_3). Since NO_2 and its degradation products are also directly harmful, threshold limit values have been introduced in many countries. The relatively low annual average limit value of 40 μg m⁻³ ($\sim$21 ppb)[1] for NO_2 in Europe is often exceeded at urban kerbside monitoring stations, although NO_x emissions were reduced significantly over the past three decades. Because of the exceedance of NO_2 limiting values in German cities even relatively modern Diesel cars (EURO IV and V) were banned from some city centers with a significant economic impact on car manufactures and

customers. Thus, other measures to reduce NO_2 concentrations are intensively discussed by the city authorities to avoid the unpopular Diesel bans.

One of the proposed measures is the photocatalytic degradation of NO_x on TiO_2 containing surfaces,[2–4] leading to the formation of adsorbed nitric acid (HNO_3) or nitrate (NO_3^-), which is finally washed off from the surface by rain.

When a semi-conductor photocatalyst is irradiated by UV-light with an energy higher than the band gap, an electron from the valence band (vb) is transferred to the conduction band (cb) leaving a hole in the valence band:

$$TiO_2 + h\nu \rightarrow h_{vb}^+ + e_{cb}^-. \quad (R1)$$

The formed charges can react with adsorbed water and oxygen forming highly reactive hydroxyl (OH), superoxide (O_2^-) and hydroperoxide (HO_2) radicals on the surface of the catalyst:[2–5]

$$h_{vb}^+ + OH^-(H_2O) \rightarrow OH(+H^+), \quad (R2)$$

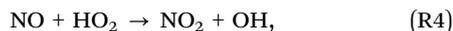$$e_{cb}^- + O_2(+H^+) \rightarrow O_2^-(HO_2). \quad (R3)$$
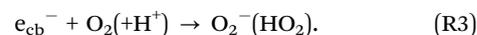
NO is mainly oxidized by the formed hydroperoxide radical to NO_2:[6]
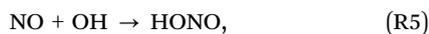
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$$NO + HO_2 \rightarrow NO_2 + OH, \tag{R4}$$

while the typical proposed oxidation of NO by OH radicals:[2,4,7–10]

$$NO + OH \rightarrow HONO, \tag{R5}$$

was excluded in the first mechanistic study, in which HONO was quantified.[6] In contrast, in the former studies,[2,4,7–10] reaction (R5) was only postulated, without experimental validation by selective HONO data.

NO_2 formed in reaction (R4) is consecutively oxidized by OH radicals to nitric acid (HNO_3) adsorbed as nitrate on the surface:[6]

$$OH + NO_2 \rightarrow HNO_3/\text{nitrate}. \tag{R6}$$

Although the photocatalytic nitrate formation is critically discussed, photocatalysis could help to improve urban air quality for different reasons:

(a) atmospheric NO_x levels will be reduced;

(b) through the accompanying photocatalytic VOC reduction both, direct (NO_2 photolysis) and indirect (photochemical smog) O_3 formation will decrease;

(c) while the absolute level of HNO_3 formation is not affected, HNO_3 formed on photocatalytic surfaces will not damage plants and the respiratory systems of animals and humans like naturally formed HNO_3 in the gas phase and, finally,

(d) if the rain wash off is further cleaned in wastewater treatment plants, even the total levels of nitrate could be reduced.

However, it is also well documented that photocatalysis can lead to the significant formation of harmful intermediates such as nitrous acid (HONO)[6,11–15] or oxygenated VOCs, like formaldehyde (HCHO),[16–21] if these commercially available surfaces are not properly designed. In addition, if the formed nitrate is not regularly washed off, photocatalysis of the adsorbed nitrate can lead to renoxification and to additional O_3 formation.[14,22] Finally, since the expected average NO_x reductions when applying photocatalytic surfaces in typical urban street canyons will be limited to a few percent,[23,24] photocatalysis should be taken only as one measure among others to improve urban air quality.

Modeling of typical average NO_x reductions by photocatalysis under urban conditions is highly uncertain since photocatalytic degradation of NO_x strongly depends on many variables, like concentration, humidity, UV irradiance and surface temperature. While the first three variables have been often tested in former laboratory studies, the influence of temperature on the uptake of NO and NO_2 and on the product formation were investigated only in a few controversial studies. However, detailed knowledge about the temperature dependence is of paramount importance, since urban surfaces (streets, walls, roofs etc.) can significantly heat up when irradiated by sunlight, especially during summertime.[25]

A positive temperature dependence of the photocatalytic oxidation of NO was observed for concrete surfaces.[10] Very recently, similar results were observed for photocatalytic roofing granules and aluminum plates coated with a pure TiO_2 photocatalyst (P25). Here, more efficient NO abatement was observed at 60 °C compared to room temperature.[25] Both studies are in contradiction with decreasing NO removal rates observed on photocatalytic mortar when the temperature was increased from 21 °C to 30 °C.[26] Also on a photocatalytic cementitious coating the reaction of NO showed a negative temperature dependence from 30 °C to 40 °C at low humidity (20% RH).[27] Moreover, in an outdoor study decreasing NO_x degradation on concrete was observed with increasing temperature.[8]

A negative temperature dependence was also observed for the uptake of NO_2 on aluminum plates coated with a pure TiO_2 photocatalyst (P25) when the surface temperature was increased from 25° to 60 °C.[25] In contrast, for the same catalyst (P25) an increasing uptake of NO_2 and decreasing HONO yields were observed with increasing temperature in a low pressure flow tube under dry conditions (buffer gas He).[28,29] A qualitatively similar temperature dependence of the NO_2 uptake was observed on an indoor photocatalytic paint, while the HONO yields were found to increase with temperature in this environmentally more realistic study.[30] However, the absolute water vapor pressure was kept constant, leading to decreasing relative humidity on the surface with increasing surface temperature. Since it is well known that the NO_2 uptake is controlled by the amount of adsorbed water on the photocatalyst, which is a function of the relative humidity,[6] the observed temperature dependence[30] may be controlled by the relative humidity and not by the temperature itself. The missing decoupling of the temperature- and humidity dependencies may also explain the controversial literature results for NO and NO_2 described above.

To carefully decouple both effects for the first time, in the present study both, the influence of the relative humidity and the temperature on the uptake of NO, NO_2 and HONO and the corresponding product yields were studied on a commercial photocatalytic dispersion paint. The pure temperature dependencies at fixed relative humidity were derived from the parameterizations of the humidity dependencies at different temperatures. Finally, complete descriptions of the temperature and humidity dependencies for NO, NO_2 and HONO were derived from the experimental data.

2 Experimental

The used paint (StoPhotosan NOx dispersion paint, white) was already applied in a former study and showed a high photocatalytic activity against NO, NO_2 and HONO.[6] Details of the paint and its preparation are explained in the ESI,† Section S1.

The photocatalytic activity of the sample was studied in a temperature-controlled (10–50 °C) flow photoreactor which is adapted to ISO 22197-1,[31] see Fig. S1 (ESI†). However, in contrast to the ISO standard, the geometry of the reactor, the experimental conditions and the data evaluation were significantly improved, as explained in detail elsewhere.[32] In contrast to the original ISO method, which considers zero order kinetics,[31–33] uptake coefficients of NO, NO_2 and HONO were calculated assuming first order kinetics:

$$\gamma = \frac{4 \cdot \ln\left(\dfrac{c_{t=0}}{c_t}\right) \cdot \Phi_g}{S \cdot \bar{v}}, \tag{1}$$

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for which $c_{t=0}$ and c_t are the mixing ratios [ppb] at the inlet and exit of the photoreactor, respectively, Φ_g is the gas flow rate [cm^3 s^{-1}], S the surface area of the sample [cm^2] and $\bar{v}$ the average velocity of the reactants [cm s^{-1}] according to the gas kinetic theory ($\bar{v} = (8RT\pi^{-1}$ M$^{-1})^{0.5}\cdot100$; with: $R = 8.314$ J mol^{-1} K^{-1}, T: absolute temperature [K] and M: molar mass [kg mol^{-1}]).

The samples were irradiated by a calibrated diode array (QUMA-Elektonik & Analytik, Wuppertal), allowing variable UVA irradiance levels between 1–16 W m^{-2}, see ESI,† Section S2.

Nitrogen oxides (NO$_x$ = NO + NO$_2$) were measured by chemiluminescence detection of NO using a molybdenum converter for NO$_2$ conversion (Eco-Physics CLD 899Y, detection limit: 25 ppt). HONO was measured by a sensitive and selective LOPAP instrument (Long Path Absorption Photometer), which is explained in detail elsewhere.[34,35] The temperature of the paint surface was measured by a calibrated thermocouple (Omega Engineering GmbH, Type K, 0.5 mm diameter, accuracy ±0.5 K), while the relative humidity and the temperature of the reaction mixture behind the reactor were measured by a calibrated humidity sensor (HYTELOG-USB, Hygrosens Instruments GmbH, accuracy $\pm2\%$ RH). Further details of the instrumentation used are provided in the ESI,† Section S3.

Photocatalytic conversion of NO$_x$ was studied in the flow photoreactor using mixtures of NO and NO$_2$ diluted in synthetic air, which were humidified by passing through a temperature-controlled stripping coil operated with Millipore water. The flow rate used for the experiments of ~2.2 L min^{-1} was controlled by calibrated flow controllers. After passing the flow reactor the gas mixture was analyzed for NO$_x$ and HONO, while the humidity was determined in the excess vent (see Fig. S2, ESI†).

After the sample was placed inside the reactor, it was thermally equilibrated for *ca.* one hour. Then its blank emissions in the dark and under irradiation were determined by passing pure humidified synthetic air through the reactor. Thereafter, NO or NO$_2$ were mixed to the synthetic air. Concentrations were determined, first at the inlet of the reactor (bypass), second at the outlet of the reactor in the dark and finally under irradiation using an UVA irradiance of 2.1 W m^{-2}. The irradiance was lower than the ISO recommended 10 W m^{-2} because of the very high activity of the photocatalytic paint sample against NO at 10 W m^{-2}, especially at low relative humidity at elevated surface temperatures. For these conditions almost all the NO was photochemically oxidized and small changes in the final NO levels lead to very large uncertainties in the uptake coefficients.

The photocatalytic activity is temperature and relative humidity dependent. Since the surface temperature directly influences the relative humidity, for each temperature, a humidity dependence was studied. The range of the relative humidity was varied from very dry conditions (stripping coil temperature ~5 °C mixed with dry air) to the highest humidity possible (stripping coil operated at room temperature). High humidity was limited by the condensation of water in the Teflon lines or in the reactor at lower reactor temperatures. Thus, the relative humidity range in the reactor was limited, especially at high surface temperatures.

3 Results

3.1 Photocatalysis of NO

3.1.1 Humidity dependence: general observations. For each temperature used (bath temperatures: 10/20/30/40/50 °C) humidity dependencies of the NO photocatalysis were investigated. As an example, the experiment with an average surface temperature of 20.6 °C is shown in Fig. 1. In the dark no significant uptake of NO was observed (~10:00–11:00 h) independent of the humidity and temperature. Thus, for the other humidities investigated the measured concentration in the dark reactor ($c_{t(\text{dark})}$) was considered equal to the bypass concentration (c_0).

There is some HONO formation on the sample in the dark reactor, which is explained by the heterogeneous conversion of NO$_2$, which was present in the NO mixtures as impurity:

$$2\ NO_2 + H_2O \rightarrow HONO + HNO_3. \qquad (R7)$$

HONO formation by reaction (R7) is plausible, since HONO levels in the dark increased with increasing humidity (see Fig. 1). In addition, HONO formation in the dark was much smaller when investigating NO compared to the NO$_2$ experiments (see Section 3.2). Since HONO formation is proposed here by the NO$_2$ reaction (R7), dark formation of HONO will be discussed below for the experiments using pure NO$_2$.

Under irradiation a strong uptake of NO was observed, which increased with decreasing humidity (see Fig. 2), in good agreement with our former study for this paint.[6] The negative humidity dependence was parameterized by 3rd order polynomials and is explained by increasing adsorption of water. Adsorbed water blocks active sites for the reaction of NO with photocatalytically formed HO$_2$ radicals, see reaction (R4).[6]

To allow fitting of the full humidity range by the 3rd order polynomials and to avoid artificial negative values for high humidity, additional theoretical activities of zero at 100% RH were added to the plots. Missing photocatalytic activity at very high RH is reasonable, since for multilayer adsorption of water no activity of the catalysts against NO is expected.[6] This was
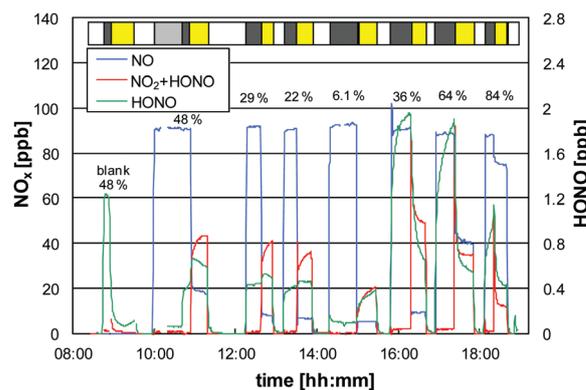

Fig. 1 Typical experiment studying the humidity dependence of the photocatalytic degradation of NO at 20.6 °C. The bars on the top of the diagram indicate the different experimental conditions: white: zero; light grey: bypass; dark grey: reactor dark; yellow: reactor + UV. The % numbers in the diagram reflect the relative humidity using the surface temperature of the sample.
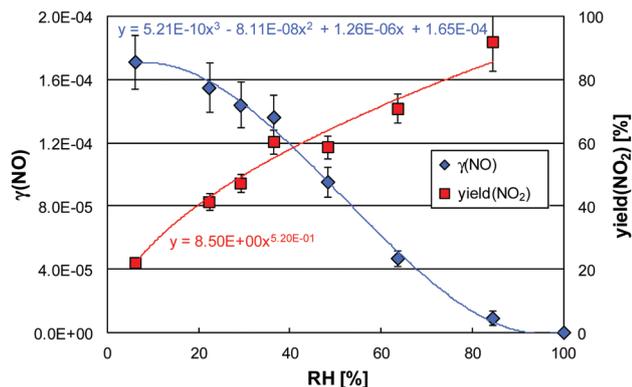
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Fig. 2 Example of the uptake of NO (γ(NO)) and the NO$_2$ yield (Φ(NO$_2$)) as a function of the relative humidity for the photocatalytic decomposition of NO at 20.6 °C (data from Fig. 1).

important, especially when only limited humidity ranges were investigated for the higher temperatures. Here, high humidity was limited by water condensation outside the photoreactor (see Experimental section).

During irradiation significant NO$_2$ formation was observed (see Fig. 1), which is explained by reaction (R4) and its consecutive oxidation by OH radicals, reaction (R6).[6] Thus, the intermediate NO$_2$ of the following simplified consecutive sequence:

$$NO \rightarrow NO_2 \rightarrow HNO_3, \quad (R8)$$

is still not fully oxidized to HNO$_3$ for the short reaction times applied (<1 s). It should be pointed out that the yield of the intermediate product NO$_2$ (Φ(NO$_2$) = ΔNO$_2$/ΔNO $\times$ 100) is strongly decreasing with the reaction time (see reaction sequence (R8)). Thus, the results from the present work are only valid for the experimental conditions applied in the fast flow reactor. In contrast, for a continuous stirred tank reactor (CSTR), which is often used in photocatalytic studies,[33] much lower NO$_2$ yields would be observed, caused by the at least two orders of magnitude longer reaction times applied. The yield of the final end product (HNO$_3$/nitrate) was not studied here, since already in a former study[6] a nitrate yield of almost unity was observed for exactly the same paint. In addition, potential deactivation of the NO-uptake by accumulation of adsorbed nitrate was not investigated. In similar passivation experiments with NO$_2$ (see Section 3.2.1), where even more nitrate formation is expected (see sequence (R8)), negligible passivation was observed for the short exposure time of the surface to nitrogen oxides ($\sim$3 h in the experiment shown in Fig. 1).

Increasing NO$_2$ yields were observed for increasing humidity, which was parameterized by a power function (see Fig. 2). For very high humidity the NO$_2$ yield was approaching unity, i.e. NO is quantitatively converted into NO$_2$ without further oxidation to the final end product nitrate, see consecutive sequence (R8).

Reasons for the high NO$_2$ yields at high humidity are (a) the faster kinetic of the NO reaction (R4) compared to the consecutive oxidation of the intermediate NO$_2$ (reaction (R6)) and (b) a stronger humidity dependence of reaction (R6) compared to reaction (R4).

For HONO a more complex behavior was observed under irradiation. While for low humidities HONO concentrations increased with UV lamps on, a significant photocatalytic HONO uptake was observed at higher humidities (s. Fig. 1). This behavior is explained by (a) the increasing NO$_2$ levels under irradiation (precursor of HONO, see reaction (R7)) and (b) the increasing photocatalytic activity of the paint against HONO with increasing humidity.[6] Since both effects overlap, the description of HONO formation is more complex in the NO system and its photocatalytic uptake is quantitatively evaluated in the experiments using pure NO$_2$ (see Section 3.2.4).

Since HONO levels under irradiation were lower with NO compared to NO$_2$ (see Section 3.2), the typically proposed photocatalytic HONO formation by the reaction of NO with OH radicals, reaction (R5),[2,4,7–10] is considered being of minor importance for the present dispersion paint. This is confirmed by the weak humidity dependence of the HONO levels under irradiation (see Fig. 1). In contrast, if HONO were formed by reaction (R5), HONO levels under irradiation should strongly decrease with humidity, caused by the low values of γ(NO) (see Fig. 2) and the high values of γ(HONO) (see Section 3.2.4) at high humidity.

In conclusion, at typical atmospheric humidities the photocatalytic paint shows a high activity against NO and HONO. The HONO yields under irradiation (Φ(HONO) = ΔHONO/ΔNO) were low (typically $<1\%$) and below the threshold limit of $<5\%$ defined in Ifang et al.[32] for all humidities and temperatures investigated. However, for very high humidities i.e. close to 100% RH, the photocatalytic paint will not improve urban air quality. Under these conditions, the reaction kinetics of NO slows down and is only converted into the more harmful intermediate NO$_2$, without final oxidation to the desired end-product nitrate, see reaction sequence (R8).

3.1.2 Temperature dependence. From the 3rd order polynomial parameterizations of the humidity dependencies described above (see Fig. 2), for each temperature investigated both, γ(NO) and Φ(NO$_2$) were calculated for fixed humidities in the range 10–90%. These data were plotted for each humidity as a function of the temperature, which is shown in Fig. 3 for 50% RH as an example.

It is obvious that both, γ(NO) and Φ(NO$_2$) are independent of the temperature within the experimental uncertainties. This behavior was observed for all humidities. The reason for this behavior may be a missing temperature dependence of the photocatalytic formation of HO$_2$ radicals, reaction (R3), which oxidizes NO to NO$_2$, see reaction (R4). If in addition the rate of reaction (R4) is limited by the HO$_2$ formation and not by the weak adsorption of NO on the catalyst, no temperature dependence of the NO oxidation would be expected.

3.1.3 Universal Parameterization of γ(NO) with T and RH. Caused by the missing temperature dependence (see Fig. 3), γ(NO) was parameterized by a simple linear function of the temperature (see eqn (2)) for each humidity in the range 10–90% RH. The slopes (m_{RH}) and intercepts (b_{RH}) were parameterized again by 3rd order polynomials against the relative humidity:
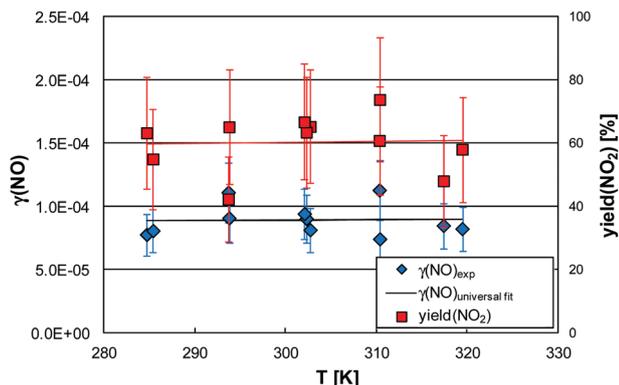
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Fig. 3 Photocatalytic activity of NO (γ(NO)), its universal parameterization (see Section 3.1.3) and the NO$_2$ yield (Φ(NO$_2$)) as a function of the temperature shown exemplarily for 50% RH. Error bars do not only represent the experimental errors but also result from uncertainties in the parameterizations of the humidity dependencies (see Fig. 2).

$$\gamma(\text{NO}) = m_{\text{RH}} \cdot T + b_{\text{RH}}, \tag{2}$$

$$m_{\text{RH}} = -2.341 \times 10^{-12} \cdot (\text{RH})^3 + 4.664 \times 10^{-10} \cdot (\text{RH})^2$$
$$- 3.005 \times 10^{-8} \cdot \text{RH} + 6.448 \times 10^{-7} \ (\text{K}^{-1}),$$

$$b_{\text{RH}} = 1.112 \times 10^{-9} \cdot (\text{RH})^3 - 1.936 \times 10^{-7} \cdot (\text{RH})^2$$
$$+ 8.145 \times 10^{-6} \cdot \text{RH} + 2.181 \times 10^{-5}.$$

Within the experimental errors eqn (2) describes the obtained data of the uptake of NO very well for all temperatures und humidities investigated (see Fig. 3 as an example). A normal Arrhenius parameterization (plot of ln(γ(NO)) against T^{-1}) has not been applied, (a) since there is practically no temperature dependence and (b) since the linear parameterization results in a better description of the experimental data.

The missing temperature dependence of the photocatalysis of NO (see Fig. 3) was derived in the present study for constant relative humidities, calculated using the surface temperature of the sample. This is in contrast to the studies by Sikkema *et al.*[10] and Tang *et al.*[25] in which positive temperature dependencies for the NO uptake were determined at fixed absolute humidities. Since the photocatalytic activity is controlled by the adsorption of water on active sites of the photocatalyst, which is a function of the relative humidity (see Fig. 2), the use of constant relative humidity is recommended to quantify the pure temperature dependence of a photocatalytic reaction.

However, the concept used in the other two studies[10,25] better describes a typical atmospheric situation, for which the surface temperature is increasing under irradiation leading to decreasing water adsorption for constant absolute humidity. If this concept would be applied in the present study, the photo-catalytic activity of the paint against NO would also strongly increase with the surface temperature (see graphical abstract). However, the reason for this result is not the temperature itself, but the decreasing relative humidity on the warmer surface, leading to decreasing levels of adsorbed water. Accordingly, when

using eqn (2), *e.g.* to model the photocatalytic decomposition of NO in the atmosphere, the surface temperature and the water vapor pressure should be known, from which the relative humidity on the surface (used in eqn (2)) can be easily calculated by the Clausius Clapeyron equation.

3.2 Photocatalysis of NO$_2$

3.2.1 Humidity dependence: general observations. Similar to NO, for each temperature used (bath temperatures: 10/20/30/40/50 °C) humidity dependencies of the NO$_2$ photocatalysis were investigated. There was already a significant uptake of NO$_2$ on the paint in the dark, which was slowing down with reaction time (see Fig. 4). In a separate experiment (data not shown), the dark uptake continuously decreased to very low values for an extended reaction time of 26 h. Thus, for simplicity, the variable dark uptake of NO$_2$ was not further studied. However, even for this extended reaction time the NO$_2$ uptake under irradiation was quite constant and was decreasing only by $\sim$15% after 26 h. Accordingly, only the total photocatalytic uptake of NO$_2$ was further evaluated from the bypass (c_0) and the reactor exit ($c_{t(\text{photo})}$) concentrations.

The slightly decreasing NO$_2$ uptake (-15% for γ(NO$_2$)) is explained by the accumulation of the adsorbed reaction product HNO$_3$/nitrate (reaction (R6)). At higher nitrate loading of the surface the increasing formation of NO$_2$ by the photocatalysis of nitrate,[14,22] leads to decreasing net NO$_2$ uptake on the surface. However, since higher NO$_2$ levels compared to the atmosphere were used in this experiment (c_0 = 140 ppb), the photocatalytic net uptake will decrease much slower in the atmosphere. Assuming a typical high urban NO$_2$ mixing ratio of 20 ppb and an exponential decrease of the NO$_2$ uptake with irradiation time, it would roughly take four completely weeks without rainfall (50% irradiation time) until the NO$_2$ uptake decrease by 30%, which is still acceptable. However, in the future this deactivation should be studied in more detail as a function of the dose of the NO$_2$ uptake or the accumulated nitrate. This data would help to
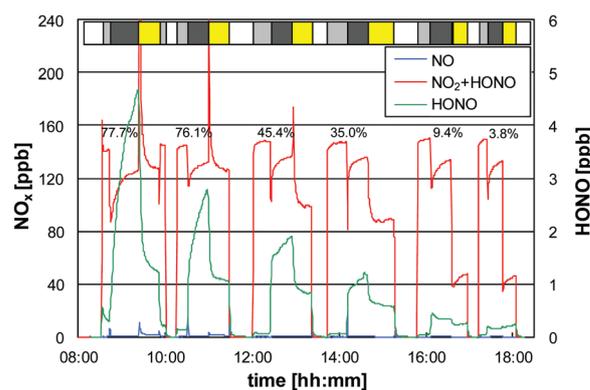

Fig. 4 Typical experiment for studying the humidity dependence of the photocatalytic degradation of NO$_2$ at 12.0 °C. The bars on the top of the diagram indicate the different experimental conditions: white: zero; light grey: bypass; dark grey: reactor dark; yellow: reactor + UV. The % numbers in the diagram reflect the relative humidity using the surface temperature of the sample.

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better model net NO_x uptake in the atmosphere for extended dry periods when the nitrate is not washed off the surfaces by rain.

In the present study, the uptake was derived for cleaned surfaces which contain only negligible amounts of adsorbed nitrate to get more reproducible results. In addition, from the 26 h experiment mentioned above, any significant reduction of the photocatalytic activity of NO_2 by accumulated nitrate can be excluded for the much shorter exposure of the surface to NO_2 when studying the humidity dependencies. Assuming an exponential decrease of the photocatalytic NO_2 uptake, a reduction of $\gamma(NO_2)$ of only 3.5% by the accumulation of nitrate can be calculated for the NO_2 exposure of ∼5.5 h in the experiment shown in Fig. 4, which is significantly smaller than the experimental error.

There is already significant formation of HONO by the dark reaction (R7) (see Fig. 4), which is increasing with humidity (see Fig. 5). Unfortunately, the reaction times applied were often not sufficient to reach steady state levels of HONO (see Fig. 4). The reaction times were chosen here only to reach almost stable NO_x levels and to finish each humidity dependency during a single day experiment. Therefore, the final HONO steady state levels were extrapolated from the concentration time profiles, leading to higher uncertainties, especially at high humidity (see error bars in Fig. 5).

In our former study, significant HONO levels in the dark were also observed for a photocatalytically non-active similar paint and explained by the porous structure and the high internal surface area.[6] For simplicity, the dark levels of HONO were parameterized by linear functions forced through the origin.

No significant NO formation was observed, neither in the dark nor under irradiation (see Fig. 4), which is reasonable with respect to the proposed reaction sequence (R8). The very small NO formation under UV irradiation especially at higher humidity (see Fig. 4) results from the photolysis of adsorbed NO_2, but not from any photocatalytic reaction as proposed in other studies.[14,36] In addition, gas phase photolysis can be excluded because of the low photolysis frequency of NO_2 ($J(NO_2) = 3.2 \times 10^{-4}$ s^{-1}) and the very short gas residence time in the photoreactor (<1 s).

Under UV irradiation the NO_2 uptake significantly increased, especially at low relative humidity (see Fig. 4), which was parameterized by an exponential function for simplicity (see Fig. 5). However, it should be pointed out that for higher surface temperatures the humidity dependence of the photocatalytic uptake significantly slows down or even decreases at low relative humidities ($<10\%$ RH), i.e. showing a maximum at ∼10% RH. This behavior is explained by reaction (R6), in which OH radicals oxidize NO_2. Since OH radicals are formed by the photocatalysis of adsorbed water, reaction (R2),[6] some humidity is necessary for the oxidation of NO_2. Only at higher humidities ($>10\%$ RH) the increasing level of adsorbed water limits the uptake of NO_2 (see similar explanation of the humidity dependence of the NO uptake). Thus, the exponential parameterization used in the present study is only valid for typical atmospheric humidities, but overestimates the uptake at $<10\%$ RH.
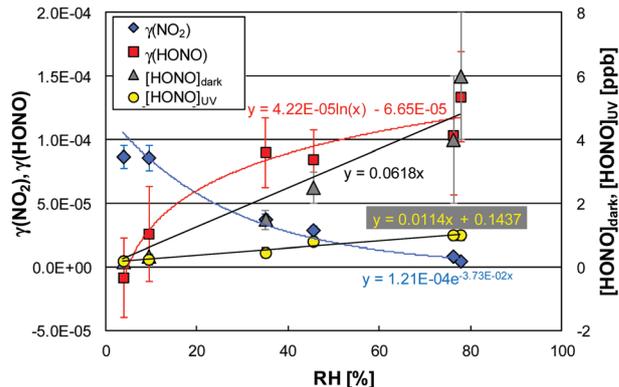

Fig. 5 Humidity dependencies of $\gamma(NO_2)$, $\gamma(HONO)$ and HONO mixing ratios in the dark and under UV irradiation derived from the data shown in Fig. 4 at 12.0 °C.

Under UV irradiation HONO levels are typically much lower compared to the dark (see Fig. 4), but still linearly increase with the relative humidity (see Fig. 5). This behavior is explained by a humidity dependent HONO formation in the dark via reaction (R7) and a photocatalytic decomposition of HONO. Caused by the increasing HONO levels in the dark (c_0) with increasing humidity, it is reasonable that the remaining HONO after photocatalytic degradation (c_t) also increase with humidity – only on a lower level. In contrast to the humidity dependence of the NO_2 uptake, the relative photocatalytic decay of HONO increases with humidity (see $\gamma(HONO)$ in Fig. 5). This behavior is explained by an oxidation of HONO as soluble nitrite in the adsorbed water layer by photocatalytically formed electron holes (h_{vb}^+):[6]

$$HONO + H_2O \leftrightarrows NO_2^- + H_3O^+; \quad (R9)$$

$$NO_2^- + 2h_{vb}^+ + H_2O \rightarrow NO_3^- + 2\,H^+,$$
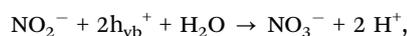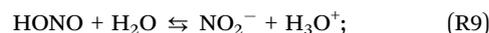
as observed from the photocatalysis of nitrite in the aqueous phase.[37]

For very dry conditions the HONO levels slightly increase with the UV lamps switched on (see Fig. 4), which is explained by additional photocatalytic HONO formation:[12]

$$NO_2 + O_2^- + H^+ \rightarrow HONO + O_2. \quad (R10)$$

Reaction (R10) becomes visible only under very dry conditions, when low HONO levels are formed by the humidity dependent dark reaction (R7) and when the photocatalytic acitivity of HONO is low (see Fig. 5). Caused by reaction (R10), the HONO levels under irradiation were parameterized by linear functions, which were not forced through the origin (see Fig. 5). Similar to our former study,[6] uptake coefficients for HONO ($\gamma(HONO)$) were derived from the dark levels of HONO (c_0) and those under irradiation (c_t) using eqn (1). This is however a simplification, since HONO formation by reactions (R7) and (R10) overlap with the photocatalytic oxidation of HONO (reaction (R9)) when passing the flow reactor. For the future, uptake experiments of pure HONO are desirable.

The photocatalytic uptake coefficients for HONO nonlinearly increase with humidity, which was parameterized by

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logarithmic functions (see Fig. 5). The artificial negative uptake coefficient at the lowest humidity shown in Fig. 5, results from the definition of the uptake coefficient (see eqn (1)) and the photocatalytic formation of HONO *via* reaction (R10). Accordingly, the parameterization of the uptake of HONO derived in the present study should not be applied for RH < 15%.

In conclusion, for typical ambient humidities the paint shows an excellent photocatalytic activity against HONO. Only for unrealistic low humidities HONO is formed from NO_2 under UV irradiation. In addition, the HONO yields under irradiation were typically smaller than the recommended threshold of <5% defined by Ifang *et al.*[32] Since HONO formation in the dark was also observed on a similar non-photocatalytic reference paint,[6] the use of this photocatalytic paint will clearly improve urban air quality with respect to the harmful pollutant nitrous acid.

3.2.2 Temperature dependence of $\gamma(NO_2)$. From the parameterizations of the humidity dependencies described above (see Fig. 5), for each temperature investigated $\gamma(NO_2)$ values were calculated for fixed humidity in the range 10–90%, and their logarithms were plotted for each humidity as a function of the inverse temperature (see Fig. 6 for 50% RH as an example). The positive slopes derived for these Arrhenius plots for each humidity ($\ln(\gamma) = \ln(A) - (E_A/R) \cdot T^{-1}$) clearly show that the uptake of NO_2 slows down with temperature. This can be explained by a temperature dependent adsorption equilibrium, $NO_{2(g)} \leftrightarrows NO_{2(ads.)}$, which is shifted to the gas phase for higher temperatures, decreasing the NO_2 uptake for the surface reaction (R6).

3.2.3 Universal parameterization of $\gamma(NO_2)$ with T and RH. From the Arrhenius plots (see Fig. 6) the slopes $(-E_A/R)_{RH}$ and intercepts $\ln(A)_{RH}$ were derived for each humidity in the range 10–90% RH and were parameterized by linear functions against the relative humidity:

$$\ln(\gamma(NO_2)) = \ln(A)_{RH}\ (-E_A/R)_{RH} \cdot T^{-1}, \qquad (3)$$

$$\ln(A)_{RH} = -0.3197 \cdot RH - 15.905,$$
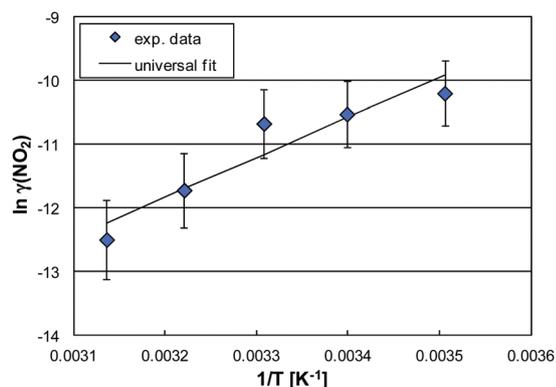
$$(-E_A/R)_{RH} = 79.426 \cdot RH + 2295.3\ (K^{-1}).$$

Fig. 6   Arrhenius plot of $\ln(\gamma(NO_2))$ *vs.* T^{-1} and its universal parameterization (see Section 3.2.3), shown for 50% RH as an example.

Within the experimental errors eqn (3) describes the data of the NO_2 uptake very well for all humidities and temperatures (see Fig. 6 for 50% RH).

The negative temperature dependence of the NO_2 photocatalysis seems to be in contradiction to results by Gandolfo *et al.*[30] who obtained a positive temperature dependence for a photocatalytic indoor paint. However, similar to the explanation of the experiments with NO, the temperature dependence of the NO_2 uptake was derived for constant relative humidities in the present study, whereas Gandolfo *et al.*[30] used fixed water vapor pressures. Since the photocatalytic activity against NO_2 is also strongly controlled by the adsorption of water on the active sites of the photocatalyst, which is a function of the relative humidity (see Fig. 5), the use of constant relative humidity is recommended to quantify the temperature dependence alone.

If constant absolute humidities were used similar to the concept of Gandolfo *et al.*, the photocatalytic activity of the paint used in the present study would also increase with the surface temperature (see graphical abstract). Accordingly, the negative temperature dependence (see Fig. 6) is overcompensated by the strong negative humidity dependence (see Fig. 5). The relative humidity is strongly decreasing with increasing surface temperature for constant water vapor pressure. Consequently, when using eqn (3), *e.g.* to model the photocatalytic decomposition of NO_2 in the atmosphere, the surface temperature and the water vapor pressure should be known, from which the relative humidity on the surface (see eqn (3)) can be easily calculated.

3.2.4 Temperature dependence of [HONO] and $\gamma(HONO)$. From the linear parameterizations of the HONO concentrations in the dark and under irradiation obtained for all temperatures (see Fig. 5) HONO levels were calculated for similar humidities in the range 15–90% and plotted against the temperature (see Fig. 7 at 50% RH as an example).

In the dark, the HONO levels exponentially increase with temperature, which can be explained by a positive temperature dependence of reaction (R7). Significant HONO formation under irradiation by reaction (R10) is of minor importance (only at RH < 15%, see above). Thus, it is plausible, that the temperature dependence of the remaining HONO after photocatalytic decomposition follows qualitatively the trend of the dark levels. However, when looking in more detail into the data shown in Fig. 7, the HONO levels under irradiation increase less with temperature compared to the dark levels, which is explained by the faster uptake of HONO with increasing temperature. To confirm this assumption the uptake coefficients of HONO were calculated for similar humidities for the different experimental temperatures applied. When plotting the data according to an Arrhenius expression, an increasing uptake is observed with increasing temperature (see Fig. 8 as an example for 50% RH).

The observed positive humidity and temperature dependencies of the photocatalytic uptake of HONO on the dispersion paint agree with the mechanism proposed by Laufs *et al.*,[6] in which HONO is oxidized in its ionic form (NO_2^-) to nitrate (NO_3^-) in a
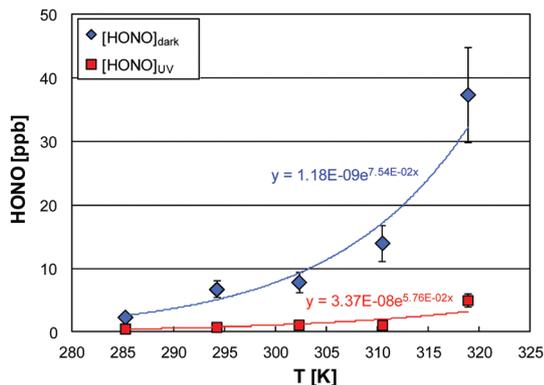
Fig. 7 Temperature dependence of the HONO mixing ratio in the dark and under UV irradiation (50% RH as an example).

layer of adsorbed water by valence band electron holes (h_{vb}^+), see reaction (9). For high humidity more HONO gets soluble explaining the positive humidity dependence of the HONO uptake. In addition, for aqueous phase ion chemistry a positive temperature dependence is also expected. In contrast, the photocatalytic oxidation of adsorbed molecular HONO by OH radicals, typically proposed in the literature:[2,4,10]

$$HONO + OH \rightarrow NO_2 + H_2O, \qquad (R11)$$
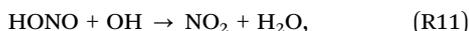
is expected to be of minor importance because of by the positive humidity dependence of the HONO uptake. Assuming adsorbed molecular HONO as reactant, reaction (R11), a negative humidity dependence would be expected similar to those observed for NO and NO_2, which is explained by the blocking of active adsorption sites with water.

The positive humidity (see Fig. 5) and temperature (see Fig. 8) dependencies of the HONO uptake on the dispersion paint are in contrast to a recent study in which negative humidity and temperature dependencies were observed for the photocatalytic uptake of HONO on a pure TiO₂ photocatalyst (P25) in a low pressure flow tube.[38] It could be speculated that the different experimental conditions (low pressure *vs.* atmospheric pressure; He *vs.* synthetic air as buffer gas; different humidity levels; *etc.*) but also the different acidities of the
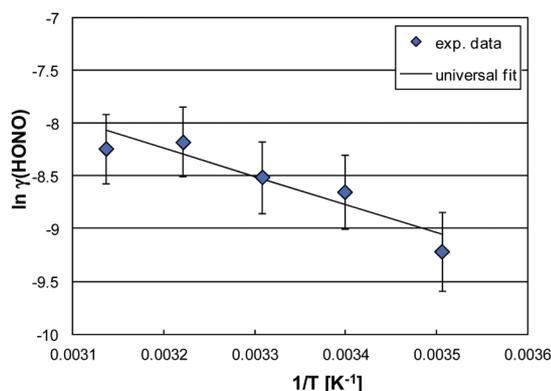
surfaces used caused the different observations. The pure P25 TiO₂ photocatalyst used by El Zein *et al.*[38] shows slightly acidic surfaces properties, favoring adsorbed undissociated HONO as reactant. In contrast, the surface of the present dispersion paint is alkaline (pH 8–8.5). Accordingly, adsorbed HONO will be efficiently converted into nitrite, see equilibrium (R9). Consequently, photocatalysis should be studied not only on pure TiO₂ surfaces, but more importantly also on real commercially available photocatalytic substrates such as concrete, paints, self-cleaning glass, *etc.*

3.2.5 Universal parameterization of γ(HONO) with T and RH. Similar to the results with NO and NO_2, γ(HONO) was parameterized from the humidity dependence of the slopes and intercepts of the temperature dependence (see Fig. 8) leading to a universal parameterization of γ(HONO):

$$\ln(\gamma(HONO)) = \ln(A)_{RH}(-E_A/R)_{RH} \cdot T^{-1}, \qquad (4)$$

$$\ln(A)_{RH} = 506.81 \cdot RH^{-1.556} - 0.85,$$

$$(-E_A/R)_{RH} = -1.292 \times 10^5 \cdot (RH)^{-1.420} - 2170 \ (K^{-1}).$$

Within the experimental errors all uptake data of γ(HONO) can be described well by eqn (4) (see Fig. 8 as an example for 50% RH). The parameterization can be used to model photocatalytic HONO uptake on urban surfaces under any experimental condition.

When constant water vapor pressure is assumed, γ(HONO) calculated by eqn (4) is almost independent of the surface temperature of the paint (see graphical abstract). Here, the positive temperature dependence of γ(HONO) for constant relative humidity (see Fig. 8) is compensated by a decreasing uptake with decreasing relative humidity (see Fig. 5) at higher temperatures. Accordingly, in the atmosphere, the uptake of HONO is independent of the temperature when photocatalytic surfaces are heated by irradiation with sunlight at constant water vapour pressure.

Since HONO formation and uptake were studied only indirectly in the NO_2 experiments, it is desirable to study the humidity and temperature dependencies of the photocatalysis of HONO using a pure HONO source in the future.

4 Conclusions

In the present study humidity and temperature dependencies of the photocatalytic uptake of NO, NO_2 and HONO were studied on a commercial dispersion paint in a flow reactor and decoupled for the first time. The obtained humidity dependencies were in good agreement with a former study performed at ambient temperature showing a decreasing uptake for NO and NO_2 with increasing humidity, while the opposite has been observed for HONO. The differences were explained by surface adsorption of water blocking active sites for the adsorption of NO and NO_2, while HONO is proposed to be oxidized as soluble nitrite in a film of adsorbed water on the alkaline surface of the dispersion paint.

Fig. 8 Arrhenius plot of $\ln(\gamma$(HONO)) *vs.* T^{-1} and its universal parameterization as a function of T and RH (50% RH as an example).

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In addition to the former study, negligible/negative temperature dependencies are observed for the uptake of NO/NO$_2$ at constant relative humidities, respectively. In contrast, the photocatalytic uptake of HONO increases with temperature. The uptake was parameterized as a function of both, relative humidity and temperature for all species investigated. Since in addition the uptake was found to be first order at low atmospheric relevant NO$_x$ levels, the parameterizations can be used to better describe photocatalytic remediation in atmospheric chemistry-transport models under various conditions of c, RH and T.

Since the missing/negative temperature dependencies of the photocatalysis of NO/NO$_2$ are overcompensated by their strong negative humidity dependencies, the atmospheric implication is a better NO$_x$ remediation when photocatalytic surfaces are heated by irradiation with sunlight. Reasons for this are not the temperature dependencies, but the strong negative humidity dependencies of the NO and NO$_2$ uptake and the decreasing relative humidity on heated surfaces.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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