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## Review of heterogeneous photochemical reactions of NO<sub>y</sub> on aerosol – A possible daytime source of nitrous acid (HONO) in the atmosphere

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### Abstract

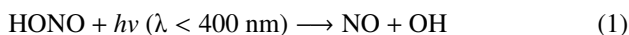
As an important precursor of hydroxyl radical, nitrous acid (HONO) plays a key role in the chemistry of the lower atmosphere. Recent atmospheric measurements and model calculations show strong enhancement for HONO formation during daytime, while they are inconsistent with the known sources in the atmosphere, suggesting that current models are lacking important sources for HONO. In this article, heterogeneous photochemical reactions of nitric acid/nitrate anion and nitrogen oxide on various aerosols were reviewed and their potential contribution to HONO formation was also discussed. It is demonstrated that HONO can be formed by photochemical reaction on surfaces with deposited HNO<sub>3</sub>, by photocatalytic reaction of NO<sub>2</sub> on TiO<sub>2</sub> or TiO<sub>2</sub>-containing materials, and by photochemical reaction of NO<sub>2</sub> on soot, humic acids or other photosensitized organic surfaces. Although significant uncertainties still exist in the exact mechanisms and the yield of HONO, these additional sources might explain daytime observations in the atmosphere.

**Key words:** atmospheric particulate matter; NO<sub>2</sub>; HONO; heterogeneous photochemical reaction

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### Introduction

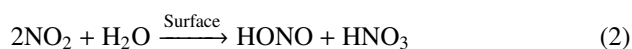
Hydroxyl radical (OH) is the primary oxidant in the atmosphere, responsible for the oxidation and removal of most natural and anthropogenic trace gases. In addition, the chemistry of the OH radical leads to the formation of harmful photo-oxidants, such as ozone and peroxyacetyl nitrate (PAN) (Kleffmann, 2007). Therefore, the formation of nitrous acid (HONO) in the atmosphere is of considerable interest since HONO is a major precursor of OH. Reaction (1) describes the main formation pathway of OH in the lower layer of the troposphere (Harrison et al., 1996; Alicke et al., 2002, 2003; Zhou et al., 2002a; Aumont et al., 2003; Ren et al., 2003; Vogel et al., 2003; Kleffmann et al., 2005; Acker et al., 2006).



This reaction contributes to 60% of the integrated OH yield (Alicke et al., 2002, 2003; Zhou et al., 2002a; Aumont et al., 2003; Ren et al., 2003; Vogel et al., 2003; Kleffmann et al., 2005). Furthermore, HONO is an indoor toxic chemical. It can also react with amines leading to nitrosamines, which are known to be mutagenic and carcinogenic (Pitts et al., 1978). Therefore, it is essential

to understand and identify the sources of tropospheric HONO.

However, the sources of HONO in the troposphere are not yet well understood. It has been generally accepted that HONO is formed predominantly by the heterogeneous reduction of NO<sub>2</sub> during nighttime, mainly through the hydrolysis reaction (Finlayson-Pitts et al., 2003; Ramazan et al., 2006, and references therein):



This reaction was discussed in detail in a review article of Finlayson-Pitts et al. (2003). It should be pointed out that Reaction (2) is not photoenhanced (Ramazan et al., 2004; George et al., 2005; Rohrer et al., 2005). The heterogeneous reaction of NO<sub>2</sub> on soot aerosol leading to the formation of HONO has attracted attention as a possible nighttime source of nitrous acid (Aumont et al., 1999), whereas the soot surface for this reaction may be rapidly deactivated via consumption of the reactive species in the dark. On the other hand, Su et al. (2011) found that the release of HONO from soil may also be important in the natural environment. Field measurements and model calculations (Staffelbach et al., 1997; Zhou et al., 2001, 2002a, 2003; Honrath et al., 2002; Kleffmann et al., 2003, 2005; Ren et al., 2003; Vogel et al., 2003;

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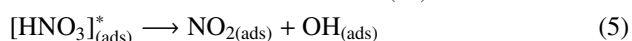
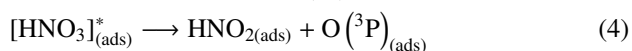
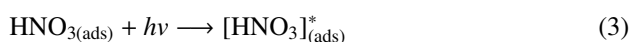
Acker et al., 2006) showed a strong enhancement for the formation of HONO during daytime (60 times higher than the nighttime sources (Kleffmann et al., 2005)). Zhou et al. (2011) found that the concentration of HONO also exhibited a significant diurnal variation pattern, with a daytime maximum of 70 pptv around noontime and a minimum of around 20 pptv around the time of sunset on forest canopies at the University of Michigan Biological Station. Unfortunately, direct emissions, gas phase formation as well as the sources mentioned above cannot explain the enhancement of HONO during daytime. Thus, the role of heterogeneous photochemical reactions should be considered. This article reviews the recent progress in the heterogeneous photochemical reactions of nitric acid/nitrate anion and nitrogen oxide on various aerosols. The potential role for these reactions in the source of HONO is discussed.

## 1 Photochemical reactions on inorganic aerosol

In the past 30 years, heterogeneous reactions of total reactive nitrogen (NO<sub>y</sub>) on mineral dust have been focused mainly on the nighttime chemistry. Usher et al. (2003) and Ma et al. (2011a) have reviewed the reaction mechanism and kinetics for this reaction system. It was well recognized that adsorbed nitrate, nitrate coatings, and deliquesced nitrate layers can be formed on the surface of dust particles by the heterogeneous reactions of gas-phase NO<sub>2</sub> and HNO<sub>3</sub> with mineral dust. These processes are therefore considered as a sink for NO<sub>2</sub> and HNO<sub>3</sub> in the troposphere. Additionally, the heterogeneous photochemistry of these adsorbed species in the daytime becomes the concern of atmospheric scientists because these photochemical processes might generate other gaseous products.

### 1.1 Photolysis of adsorbed HNO<sub>3</sub>/nitrate

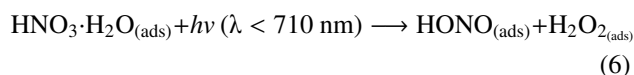
HNO<sub>3</sub> deposited on ground surfaces or glass surfaces may undergo effective photolysis to form HONO and NO<sub>x</sub>, and this reaction is 1–2 orders of magnitude faster than that in the gas phase and aqueous phase (Zhou et al., 2002b, 2003). The reaction proceeds via the following Eqs. (3)–(5):



Under humid conditions, the NO<sub>2(ads)</sub> produced on the surface may further react with H<sub>2</sub>O<sub>(ads)</sub> to produce HONO<sub>(ads)</sub>, which then can be released into the gas phase through Reaction (2). Modeling studies also suggested that HNO<sub>3</sub> photolysis was important for HONO production during the 2001 Northeast Oxidant and Particle Study (Sarwar et al., 2008). The heterogeneous photolysis of

HNO<sub>3</sub> would supply the atmosphere with a new source of photochemically reactive nitrogen species, i.e., HONO and NO<sub>x</sub>, and would thus significantly impact the chemistry of the remote low-NO<sub>x</sub> atmospheric boundary layer by altering the radical pool, as illustrated in Fig. 1.

Ramazan et al. (2004) investigated the effect of 320–400 nm radiation on HONO formation during heterogeneous NO<sub>2</sub> hydrolysis in a borosilicate glass cell at 296 K. It was found that heterogeneous hydrolysis of NO<sub>2</sub> to form HNO<sub>3</sub> is not photoenhanced. However, there is clear evidence in their experiments for the generation of gas phase HONO by photolysis of adsorbed HNO<sub>3</sub> formed by the heterogeneous hydrolysis of NO<sub>2</sub> (Reaction (2)). Adsorbed HNO<sub>3</sub> formed during the hydrolysis reaction will likely be combined with water (HNO<sub>3</sub>·H<sub>2</sub>O<sub>(ads)</sub>) on the borosilicate glass surface through hydrogen bonding (Staikova and Donaldson, 2001; McCurdy et al., 2002; Escribano et al., 2003; Fernández et al., 2003). Then, photolysis of HNO<sub>3</sub>·H<sub>2</sub>O<sub>(ads)</sub> generates HONO and H<sub>2</sub>O<sub>2</sub>, which is energetically possible with wavelengths of light below 710 nm (Ramazan et al., 2006):



The fate of the adsorbed HONO will depend in large part on the water vapor concentration, as shown in Reaction (7), in which HONO is released to the gas phase through a competitive adsorption process (Syomin and Finlayson-Pitts, 2003):



As the relative humidity (RH) is lowered, the adsorbed HONO increasingly reacts with other species such as adsorbed nitric acid and/or its complex to form NO<sub>2</sub> (the

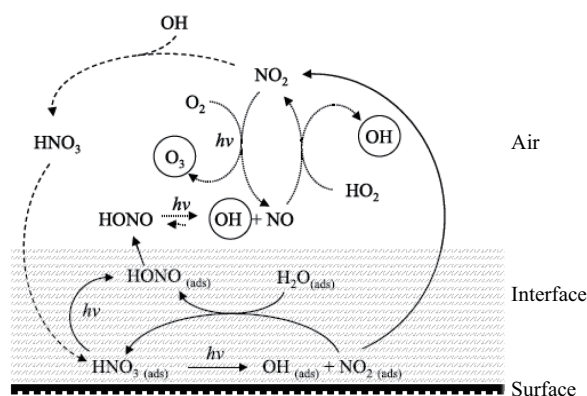
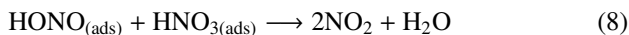


Fig. 1 Effects of the photolytic remobilization of HNO<sub>3</sub> (“re-NO<sub>x</sub>-ification”) on ground surfaces on the chemistry of the overlying atmosphere. Solid arrows are processes responsible for surface HNO<sub>3</sub> remobilization, dashed arrows indicate removal of oxidized nitrogen from the atmosphere to ground surfaces by deposition, and dotted arrows are gas-phase reactions leading to formation of O<sub>3</sub> and OH radicals (in circles) (Zhou et al., 2003).

reverse of Reaction (2)):

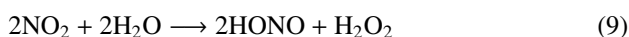


It was also found that HONO generation from the photolysis of HNO<sub>3</sub> on glass surfaces requires the presence of water, but the production rate of HONO is relatively insensitive to RH between 20% and 80% RH (Zhou et al., 2003). This can be explained by the fact that high RH is favorable to the desorption of HONO<sub>(ads)</sub> to the gas phase (Reaction (7)), while it is unfavorable to the formation of HNO<sub>3</sub>·H<sub>2</sub>O<sub>(ads)</sub> (Dubowski et al., 2004).

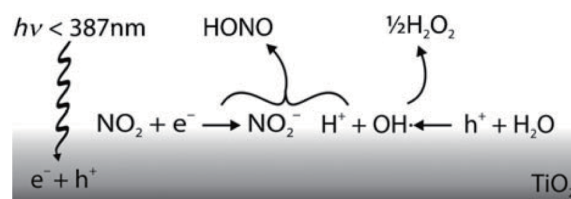
Several papers have found that surface nitrate can be formed on Al<sub>2</sub>O<sub>3</sub> through heterogeneous reactions with NO<sub>x</sub> and HNO<sub>3</sub>, photolysis of adsorbed nitrate yields only NO<sub>2</sub>, NO and N<sub>2</sub>O (Schuttlefield et al., 2008; Rubasinghe and Grassian, 2009; Chen et al., 2011). However, the formation of adsorbed HNO<sub>3</sub> on SiO<sub>2</sub> was observed when gaseous NO<sub>x</sub> reacts with SiO<sub>2</sub> (Goodman et al., 1999; Liu et al., 2012; Ma et al., 2011b). Considering the abundance of SiO<sub>2</sub> (approximately 60%) in mineral dust (Usher et al., 2003), therefore, the photolysis of adsorbed nitric acid on mineral dust or glass surfaces may be a source of HONO in the atmosphere. Additionally, field campaigns found HONO was produced by the photolysis of NO<sub>3</sub><sup>-</sup> in the snowpack and diffuses out into the air (Dibb et al., 2002, 2004; Honrath et al., 2002).

## 1.2 Photochemistry of NO<sub>2</sub> on TiO<sub>2</sub>-containing surfaces

Although being a relatively minor component of tropospheric mineral aerosols, TiO<sub>2</sub> may be of paramount importance for tropospheric daytime chemistry due to its well-known photocatalytic properties (Beaumont et al., 2009). On the other hand, TiO<sub>2</sub> nanoparticles have been used in self-cleaning window glass, building materials, and on roads in Europe, Japan and the USA. Gustafsson et al. (2006) and Beaumont et al. (2009) have investigated the heterogeneous photochemical reaction of NO<sub>2</sub> on UV-illuminated TiO<sub>2</sub> surfaces. They found that HONO and H<sub>2</sub>O<sub>2</sub> were formed from NO<sub>2</sub> and H<sub>2</sub>O under conditions pertinent to the daytime troposphere. **Figure 2** illustrates the proposed mechanism. Under UV illumination, valence electrons in TiO<sub>2</sub> are excited to the conduction band, creating valence band holes that diffuse to the surface where they split water. This process can produce OH radicals, which then combine to form H<sub>2</sub>O<sub>2</sub>. At the same time, adsorbed NO<sub>2</sub> traps the released electrons, subsequently forming HONO. The overall reaction of the proposed mechanism has been described as:



The OH source strength of 1.9 ppbv/hr could be sustained from the TiO<sub>2</sub> self-cleaning window glass-mediated photo conversion of NO<sub>2</sub> to HONO (Langridge et al., 2009). This rate is comparable to primary OH production



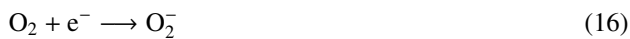
**Fig. 2** Proposed mechanism for the photocatalytic formation of nitrous acid on UV-illuminated TiO<sub>2</sub> (Beaumont et al., 2009).

from the O(<sup>1</sup>D) + H<sub>2</sub>O reaction on summer days, which is typically of 1.5 ppbv/hr (Ren et al., 2003). This finding suggests that negative environmental effects, such as generation of HONO, from the use of these TiO<sub>2</sub>-containing materials in urban areas should be evaluated systematically. It also suggests the need for field measurements of NO<sub>y</sub> levels in locations where self-cleaning materials are already being used, as well as the need for further investigation concerning these new materials.

The reaction mechanism of NO<sub>2</sub> on irradiated TiO<sub>2</sub>(x%)/SiO<sub>2</sub> films as proxies for NO<sub>x</sub> de-polluting materials were studied by Monge et al. (2010a). NO, HONO, and nitrate anions are produced as a consequence of the NO<sub>2</sub> loss on UV-illuminated TiO<sub>2</sub> films. The proposed mechanism for the obtained gas phase products is proposed as the following:

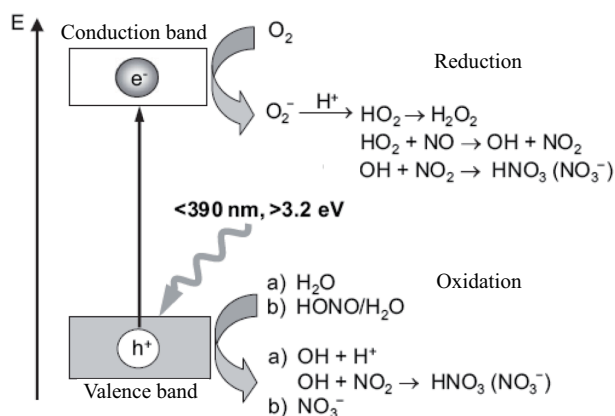


In the presence of molecular oxygen, an electron transfer to O<sub>2</sub>, which acts as the primary electron acceptor, leads to oxygen activated species which can participate in reactions as follows:



These pathways explain the higher HONO yield and lower NO yield for the heterogeneous reaction between NO<sub>2</sub> and illuminated TiO<sub>2</sub> films when O<sub>2</sub> is present in the carrier gas.

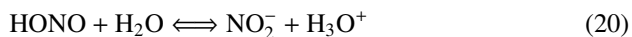
However, no gaseous HONO was formed when commercial TiO<sub>2</sub>-doped facade paints were exposed to NO<sub>x</sub> and light in a flow tube photoreactor under simulated atmospheric conditions (Laufs et al., 2010). As the main final products, adsorbed nitric acid and nitrate anions (HNO<sub>3</sub> + NO<sub>3</sub><sup>-</sup>) were observed with near unity yield. Thus, it was concluded that photocatalytic paint should not



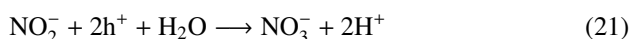
**Fig. 3** Postulated mechanism for the photocatalytic reaction of NO, NO<sub>2</sub>, and HONO on TiO<sub>2</sub>-containing photoactive paint surfaces (Laufs et al., 2010).

contribute to the daytime source of HONO. These results were opposite to the studies aforementioned. **Figure 3** shows the mechanism proposed by Laufs et al. (2010).

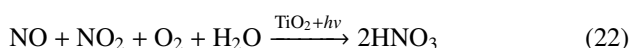
Not gas phase HONO but the solution of NO<sub>2</sub><sup>-</sup> in a film of adsorbed water was proposed:



Soluble NO<sub>2</sub><sup>-</sup> is further oxidized by electron holes to NO<sub>3</sub><sup>-</sup>:



All studied nitrogen species (NO, NO<sub>2</sub>, HONO) are photocatalytically oxidized leading to NO<sub>3</sub><sup>-</sup>, while O<sub>2</sub> is photochemically reduced. The near unity yield of NO<sub>3</sub><sup>-</sup> can be well explained by the mechanism and the following net reaction of nitrogen oxides on paint surfaces is proposed:



Since Reaction (20) is strongly dependent on pH, the lack of gaseous HONO formation can be explained by the alkaline surface properties (pH: 8–8.5) of the paints used by Laufs et al. (2010). Strongly photocatalytic HONO formation was observed on pure TiO<sub>2</sub> (Gustafsson et al., 2006), TiO<sub>2</sub>/SiO<sub>2</sub> mixtures (Ndour et al., 2008; Monge et al., 2010a) and self-cleaning window glass (Langridge et al., 2009), respectively. This may be explained by the more acidic surface properties of pure TiO<sub>2</sub> and glass materials compared to the paints used by Laufs et al. (2010), which will shift Reaction (20) to the left side, leading to low decomposition of HONO. Therefore, alkaline photocatalytic materials should be more environmentally friendly toward the removal of NO<sub>x</sub>.

Photochemical HONO formation was also observed on real atmospheric particles (Saharan dust and Arizona test dust) and this fact was also attributed to the presence of TiO<sub>2</sub> (Ndour et al., 2008). Although the amounts of TiO<sub>2</sub>

were small (≤ 1%) in these samples, it is worthwhile emphasizing that this quantity is sufficient to make these sands photochemically active. It was also found that the heterogeneous conversion of NO<sub>2</sub> into HONO on ice films containing humic acid was significantly enhanced by visible light (Bartels-Rausch et al., 2010).

From the studies reviewed here, it is concluded that photolysis of adsorbed HNO<sub>3</sub>/nitrate and photoreaction of NO<sub>2</sub> on TiO<sub>2</sub>-containing surfaces is a possible source of HONO in the daytime. However, more kinetic data which can be used in the model studies should be measured in future work. On the other hand, it is important to note that the relative humidity, the amount of molecular oxygen, the wavelength and intensity of the light, and the type of the substrate have an important effect on the heterogeneous photochemical reaction of NO<sub>x</sub>. Therefore, further kinetic studies under atmospherically relevant conditions are necessary to better understand the photochemistry of NO<sub>y</sub> in the atmosphere.

## 2 Photochemical reactions on organic aerosol

The heterogeneous reaction of NO<sub>2</sub> on soot aerosol has attracted much attention because this reaction leads to the formation of HONO and is considered as a possible nighttime source of HONO (Aumont et al., 1999). Soot aerosol, which consists primarily of elemental carbon with a variable fraction of organic materials, is ubiquitous in the atmosphere and comprises about 10%–50% of the total tropospheric particulate matter (Ackerman et al., 2000; Jacobson, 2001; Chameides and Bergin, 2002; Zhang et al., 2008) and may provide a significant fraction of available aerosol reaction surface due to its fractal morphology. Because of its atmospheric relevance, the heterogeneous conversion of NO<sub>2</sub> to HONO has been extensively studied in the laboratory for a broad range of NO<sub>2</sub> concentrations on a variety of carbonaceous materials, including spark discharge soot (Ammann et al., 1998; Kalberer et al., 1999), hydrocarbon flame soot (Gerecke et al., 1998; Kleffmann et al., 1999; Al-Abadleh and Grassian, 2000; Stadler and Rossi, 2000; Salgado and Rossi, 2002; Lelièvre et al., 2004; Kleffmann and Wiesen, 2005; Aubin and Abbatt, 2007; Khalizov et al., 2010), commercial black carbon (Kleffmann et al., 1999; Kleffmann and Wiesen, 2005), diesel soot (Arens et al., 2001), etc. Depending on the measurement technique, type of soot, assumed surface area, and initial concentration of NO<sub>2</sub>, the reported uptake coefficients vary over 7 orders of magnitude, from 10<sup>-1</sup> to 10<sup>-8</sup>, and HONO yields vary from a few percent to about 100%. However, in the dark, soot surfaces are rapidly deactivated under atmospheric conditions, leading to the understanding that soot affects the tropospheric concentration of HONO only in a minor way.

Recently, Monge et al. (2010b) found that the conversion of NO<sub>2</sub> to HONO on soot particles was dramatically

enhanced in the presence of artificial solar radiation, and led to persistent reactivity over time scales comparable to the lifetime of soot in the atmosphere. Based on their results, a HONO production rate of 25 pptv/hr would be expected as a lower limit value for an urban environment with soot deposited on urban surfaces. These results challenge the current view of the negligible importance of soot chemistry with respect to the troposphere composition due to its rapid surface deactivation in the dark. However, only the interaction between soot and UV-A radiation has been investigated so far while the effect of visible light has not been quantified yet. Therefore, more studies on soot photochemistry are needed in the future.

HONO was detected as a gas-phase product in the heterogeneous reaction between gaseous NO<sub>2</sub> and solid pyrene/KNO<sub>2</sub> films, which were used as a simplified proxy of urban grime (Ammar et al., 2010). From this result, a HONO production rate of 130 pptv/hr would be expected as a conservative estimate assuming that only 1% of a street canyon surface with 10 m street width and 20 m building

height is covered by pyrene/nitrate films. Brigante et al. (2008) also deduced that photoexcited pyrene may reduce NO<sub>2</sub> to HONO and NO, with yields of ca. 15% and ca. 30%, respectively.

The reactivity and HONO yields for the reaction of NO<sub>2</sub> with organic films of different compositions in the dark and under irradiation (light in the range 300–420 nm) are shown in **Table 1** (George et al., 2005). The uptake coefficients observed here easily reach 10<sup>-6</sup> or higher, with HONO yields between 50% and close to 100% with an artificial irradiance comparable to the solar irradiance in the wavelength interval of 300–420 nm at the Earth surface under 0° zenith angle.

The stoichiometry of the formation of HONO from NO<sub>2</sub> in the 4-benzoylbenzoic acid (4-BBA) photosensitized reaction (**Table 1**) with a HONO yield up to 100% shows that this reaction cannot be explained as a catalyzed disproportionation of NO<sub>2</sub> on wet surfaces (Reaction (2), see introduction). Therefore, the primary electron donor must be a constituent of the organic films. The light is

**Table 1** Reactivity and HONO yields of the reaction of NO<sub>2</sub> with organic films of different compositions in the dark and under irradiation (300–420 nm) (George et al., 2005)

| Type of organic coating and amount of organic compound used | Removal of initial [NO <sub>2</sub> ] by dark reaction <sup>b</sup> (%) | Yield of HONO per reacted NO <sub>2</sub> in dark reaction (%) | Removal of initial [NO <sub>2</sub> ] by light reaction <sup>cd</sup> (%) | Yield of HONO per reacted NO <sub>2</sub> in light reaction (%) |
|---|---|--|---|---|
| Sodium 4-benzoylbenzoate (1 mg)                             | 4   | 7  | 20/17   | 45/48   |
| 4-Benzoylbenzoic acid (1 mg)                                | 2   | n.a.   | 12/12   | 68/71   |
| 3,7-Dihydroxy-2-naphthoic acid (1 mg)                       | 4   | 11   | 22/28/38 <sup>e</sup>   | 67/74/77  |
| Perylene (0.5 mg)   | 3   | n.a.   | ~0/0  | n.a.  |
| Syringic acid (1 mg)  | 6   | 6  | 7/7   | 36/43   |
| 3,4-Dihydroxyphenylacetic acid (1 mg)                       | 6   | n.a.   | 1/2   | n.a.  |
| Potassium iodide (1 mg)                                     | 53  | 100  | ~0/0  | n.a.  |
| External mixture <sup>a</sup>                               | 4   | 4  | 36/36   | 61/70   |
| Sodium 4-benzoylbenzoate (1 mg)                             |   |  |   |   |
| Syringic acid (0.5 mg)                                      |   |  |   |   |
| External mixture <sup>a</sup>                               | 2   | n.a.   | 42/38   | 91/90   |
| Sodium 4-benzoylbenzoate (1 mg)                             |   |  |   |   |
| 3,4-Dihydroxyphenylacetic acid (1 mg)                       |   |  |   |   |
| External mixture <sup>a</sup>                               | 14  | n.a.   | 66/58   | 93/101  |
| Sodium 4-benzoylbenzoate (1 mg)                             |   |  |   |   |
| Potassium iodide (1 mg)                                     |   |  |   |   |
| External mixture <sup>a</sup>                               | 2   | n.a.   | 6/9   | 57/67   |
| Perylene (0.5 mg)   |   |  |   |   |
| 3,4-Dihydroxyphenylacetic acid (1 mg)                       |   |  |   |   |
| External mixture <sup>a</sup>                               | 20  | > 80   | 7/10  | n.a.  |
| Perylene (0.5 mg)   |   |  |   |   |
| Potassium iodide (1 mg)                                     |   |  |   |   |
| Internal mixture <sup>a</sup>                               | 16  | n.a.   | 52/63   | 90/93   |
| 4-Benzoylbenzoic acid (1 mg)                                |   |  |   |   |
| 3,4-Dihydroxyphenylacetic acid (0.5 mg)                     |   |  |   |   |
| Internal mixture <sup>a</sup>                               | 7   | n.a.   | 47/58   | 95/97   |
| 4-Benzoylbenzoic acid (1 mg)                                |   |  |   |   |
| 3,4-Dihydroxyphenylacetic acid (1 mg)                       |   |  |   |   |

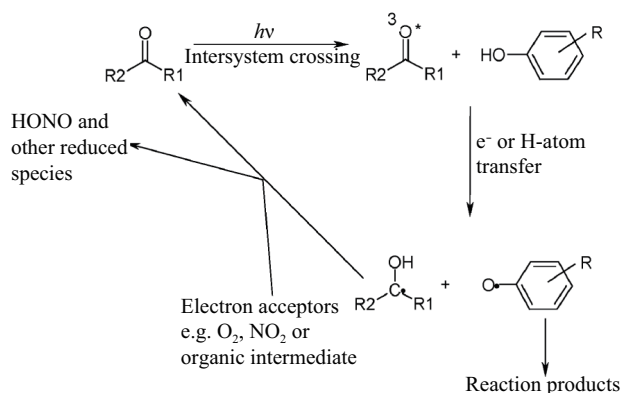
<sup>a</sup> The term external mixture is used when the reactor surface was coated first by the absorber molecule and subsequently by the phenol or potassium iodide. The term internal mixture is used when the reactor was coated from one solution containing both compounds.

<sup>b</sup> The removal of NO<sub>2</sub> due to the dark reaction was measured by exposing the coated wall reactor to the NO<sub>2</sub>-mixture and measuring the decrease of the NO<sub>2</sub> concentration.

<sup>c</sup> The removal of NO<sub>2</sub> due to the light reaction was measured by illuminating the NO<sub>2</sub>-mixture flowing through the coated wall reactor and comparing the NO<sub>2</sub> concentration before and during the irradiation.

<sup>d</sup> Values after 5 and 10 min of irradiation, respectively.

<sup>e</sup> Values after 5, 10 and 25 min of irradiation, respectively.



**Fig. 4** Proposed reaction mechanism for the photoreduction of NO<sub>2</sub> to HONO in the presence of 4-BBA (absorbing photosensitizer) and a substituted phenol (electron donor) (George et al., 2005).

primarily absorbed by 4-BBA and the proposed mechanism is depicted in **Fig. 4**. Organic substrates containing a combination of electron donors, such as phenols, and of compounds yielding excited triplet states, such as aromatic ketones, showed a high reactivity towards NO<sub>2</sub>.

Humic substances are the most abundant group of organic species on the Earth surface (Batjes, 1996; Swift, 2001; Janzen, 2004). They stem from the degradation of biological materials. As humic matter is ubiquitously found on ground surfaces, it is likely that such materials also exist in aerosols (due to soil abrasion or biomass burning). On the other hand, atmospheric oxidation of VOC is another source of humic-like substances (similar polymeric particle-bound materials) present in aerosols (Jang et al., 2002; Kalberer et al., 2004). More specifically, aromatic compounds typically present in biomass burning aerosols may undergo oxidation processes that lead to products similar to humic acids (Gelencsèr et al., 2003).

In the dark, the formation of HONO from the reaction of NO<sub>2</sub> with humic acid aerosols (Stemmler et al., 2007) or secondary organic aerosol surfaces (Bröske et al., 2003) was below the detection limit, corresponding to an uptake coefficient  $\gamma_{\text{rxn}} < 10^{-7}$ . Stemmler et al. (2006) found that soil and other films containing humic acid (HA) exhibit an organic surface photochemistry that produces reductive surface species, which can react selectively with NO<sub>2</sub> to form HONO.



where, A<sup>red</sup> is photo-produced reductive centers, X<sup>ox</sup> is photo-oxidants.

However, they cannot yet assign the exact chemical nature of the reducing intermediates formed on the irradiated HA film. The formation of HONO occurs not only in the UV-A spectral region, but also in the visible region under atmospheric conditions. The observed rate of HONO formation could explain the recently observed

high daytime concentration of HONO in the boundary layer and could be predicted to have a large contribution (for example, 20%–30%) to the hydroxyl radical production of the lowest hundred to a few hundred meters of the atmosphere. However, Stemmler et al. (2007) also found the formation of HONO on submicron humic acid aerosol, but the measured uptake coefficients for the NO<sub>2</sub> to HONO conversion are too low to explain the HONO formation rates observed near the ground in rural and urban environments by the conversion of NO<sub>2</sub> to HONO on organic aerosol surfaces, even if one assumes that all aerosols consist of humic acid only. It should be pointed out that the humic acid material used in these studies may have a higher photo-reactivity than authentic humic substances. Therefore, the values mentioned above should be considered as upper limits. The kinetic data should be measured under real atmospheric environment conditions in the future. On the other hand, the reaction mechanism of NO<sub>2</sub> with organic materials needs to be confirmed.

### 3 Conclusions and outlook

Heterogeneous photochemical reactions of nitric acid/nitrate anion or nitrogen oxide on various aerosols as potential sources of HONO were reviewed in this article. Three different new photochemical sources of HONO have been discovered, that is, HONO formation by photochemical reaction on surfaces with deposited HNO<sub>3</sub>, by photocatalytic reaction of NO<sub>2</sub> on TiO<sub>2</sub> or TiO<sub>2</sub>-containing materials, and by photochemical reaction on soot, humic acids or other photosensitized organic surfaces. Although significant uncertainties still exist concerning the exact mechanisms and the yield of HONO, these previous results imply that heterogeneous photoreactions on aerosol might explain the source of OH in the daytime. Of course, further studies are still needed and should include the following:

(1) Since HONO is a major precursor of atmospheric hydroxyl radicals, it makes a high contribution to the oxidation capacity of the atmosphere. The concentration of HONO should be routinely measured in field observations.

(2) Further laboratory studies on the photochemical formation of HONO are necessary to better understand and to predict HONO formation in the atmosphere. The mechanism of the photochemical HONO formation on soot or humic acid aerosols should be clarified. The contribution of main sources to the concentration of HONO should also be confirmed. For example, Sarwar et al. (2008) suggested that heterogeneous reactions and surface photolysis reactions accounted for about 86% of the predicted HONO, while emissions and gas-phase reactions accounted for only 14% of the predicted HONO using the Community Multiscale Air Quality modeling system.

(3) Up to now, most climate models did not consider the effect of light on the heterogeneous reactivity of atmo-



spheric trace gases on aerosols. Therefore, the contribution of atmospheric heterogeneous photochemistry should be considered in these models.

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