



Review of heterogeneous photochemical reactions of NO_y on aerosol – A possible daytime source of nitrous acid (HONO) in the atmosphere

Jinzhu Ma, Yongchun Liu, Chong Han, Qingxin Ma, Chang Liu, Hong He*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: jzma@rcees.ac.cn

Received 07 June 2012; revised 27 September 2012; accepted 11 October 2012

Abstract

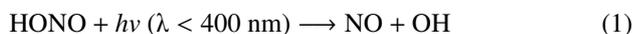
As an important precursor of hydroxyl radical, nitrous acid (HONO) plays a key role in the chemistry of the lower atmosphere. Recent atmospheric measurements and model calculations show strong enhancement for HONO formation during daytime, while they are inconsistent with the known sources in the atmosphere, 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 HNO₃, by photocatalytic reaction of NO₂ on TiO₂ or TiO₂-containing materials, and by photochemical reaction of NO₂ 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; NO₂; HONO; heterogeneous photochemical reaction

DOI: 10.1016/S1001-0742(12)60093-X

Introduction

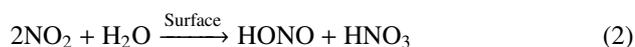
Hydroxyl radical (OH) is the primary oxidant in the atmosphere, responsible for the oxidation and removal of most natural and anthropogenic trace gases. In addition, the chemistry of the OH radical leads to the formation of harmful photo-oxidants, such as ozone and peroxyacetyl nitrate (PAN) (Kleffmann, 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 NO₂ 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 NO₂ 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;

* Corresponding author. E-mail: honghe@rcees.ac.cn

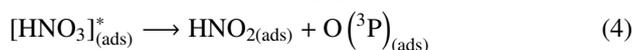
Acker et al., 2006) showed a strong enhancement for the formation of HONO during daytime (60 times higher than the nighttime sources (Kleffmann et al., 2005)). Zhou et al. (2011) found that the concentration of HONO also exhibited a significant diurnal variation pattern, with a daytime maximum of 70 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_y) 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 NO₂ and HNO₃ with mineral dust. These processes are therefore considered as a sink for NO₂ and HNO₃ 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 HNO₃/nitrate

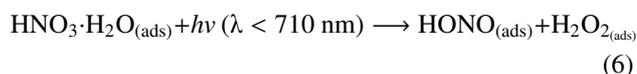
HNO₃ deposited on ground surfaces or glass surfaces may undergo effective photolysis to form HONO and NO_x, and this reaction is 1–2 orders of magnitude faster than that in the gas phase and aqueous phase (Zhou et al., 2002b, 2003). The reaction proceeds via the following Eqs. (3)–(5):



Under humid conditions, the NO_{2(ads)} produced on the surface may further react with H₂O_(ads) to produce HONO_(ads), which then can be released into the gas phase through Reaction (2). Modeling studies also suggested that HNO₃ photolysis was important for HONO production during the 2001 Northeast Oxidant and Particle Study (Sarwar et al., 2008). The heterogeneous photolysis of

HNO₃ would supply the atmosphere with a new source of photochemically reactive nitrogen species, i.e., HONO and NO_x, and would thus significantly impact the chemistry of the remote low-NO_x 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 NO₂ hydrolysis in a borosilicate glass cell at 296 K. It was found that heterogeneous hydrolysis of NO₂ to form HNO₃ is not photoenhanced. However, there is clear evidence in their experiments for the generation of gas phase HONO by photolysis of adsorbed HNO₃ formed by the heterogeneous hydrolysis of NO₂ (Reaction (2)). Adsorbed HNO₃ formed during the hydrolysis reaction will likely be combined with water (HNO₃·H₂O_(ads)) 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 HNO₃·H₂O_(ads) generates HONO and H₂O₂, 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 NO₂ (the

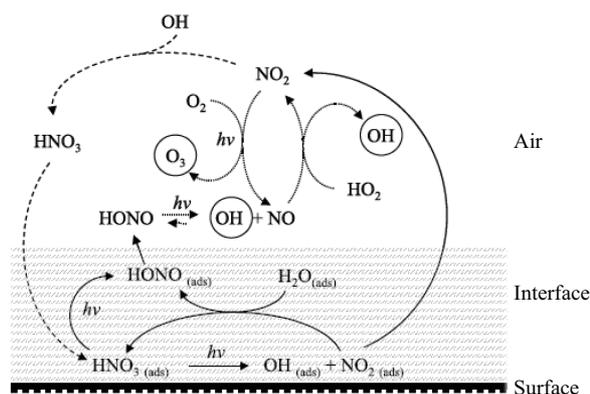
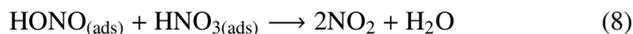


Fig. 1 Effects of the photolytic remobilization of HNO₃ (“re-NO_x-ification”) on ground surfaces on the chemistry of the overlying atmosphere. Solid arrows are processes responsible for surface HNO₃ remobilization, dashed arrows indicate removal of oxidized nitrogen from the atmosphere to ground surfaces by deposition, and dotted arrows are gas-phase reactions leading to formation of O₃ and OH radicals (in circles) (Zhou et al., 2003).

reverse of Reaction (2)):

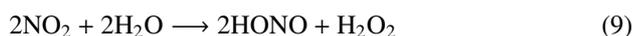


It was also found that HONO generation from the photolysis of HNO₃ on glass surfaces requires the presence of water, but the production rate of HONO is relatively insensitive to RH between 20% and 80% RH (Zhou et al., 2003). This can be explained by the fact that high RH is favorable to the desorption of HONO_(ads) to the gas phase (Reaction (7)), while it is unfavorable to the formation of HNO₃·H₂O_(ads) (Dubowski et al., 2004).

Several papers have found that surface nitrate can be formed on Al₂O₃ through heterogeneous reactions with NO_x and HNO₃, photolysis of adsorbed nitrate yields only NO₂, NO and N₂O (Schuttlefield et al., 2008; Rubasinghe and Grassian, 2009; Chen et al., 2011). However, the formation of adsorbed HNO₃ on SiO₂ was observed when gaseous NO_x reacts with SiO₂ (Goodman et al., 1999; Liu et al., 2012; Ma et al., 2011b). Considering the abundance of SiO₂ (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 NO₃⁻ in the snowpack and diffuses out into the air (Dibb et al., 2002, 2004; Honrath et al., 2002).

1.2 Photochemistry of NO₂ on TiO₂-containing surfaces

Although being a relatively minor component of tropospheric mineral aerosols, TiO₂ may be of paramount importance for tropospheric daytime chemistry due to its well-known photocatalytic properties (Beaumont et al., 2009). On the other hand, TiO₂ 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 NO₂ on UV-illuminated TiO₂ surfaces. They found that HONO and H₂O₂ were formed from NO₂ and H₂O under conditions pertinent to the daytime troposphere. **Figure 2** illustrates the proposed mechanism. Under UV illumination, valence electrons in TiO₂ 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 H₂O₂. At the same time, adsorbed NO₂ 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 TiO₂ self-cleaning window glass-mediated photo conversion of NO₂ to HONO (Langridge et al., 2009). This rate is comparable to primary OH production

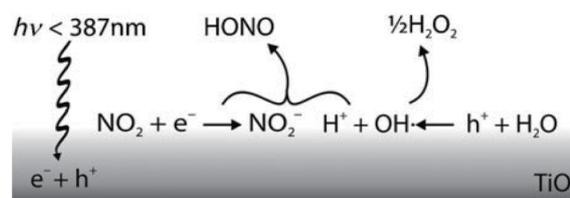


Fig. 2 Proposed mechanism for the photocatalytic formation of nitrous acid on UV-illuminated TiO₂ (Beaumont et al., 2009).

from the O(¹D) + H₂O 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 TiO₂-containing materials in urban areas should be evaluated systematically. It also suggests the need for field measurements of NO_y 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 NO₂ on irradiated TiO₂(x%)/SiO₂ films as proxies for NO_x de-polluting materials were studied by Monge et al. (2010a). NO, HONO, and nitrate anions are produced as a consequence of the NO₂ loss on UV-illuminated TiO₂ 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 O₂, 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 NO₂ and illuminated TiO₂ films when O₂ is present in the carrier gas.

However, no gaseous HONO was formed when commercial TiO₂-doped facade paints were exposed to NO_x 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 (HNO₃ + NO₃⁻) were observed with near unity yield. Thus, it was concluded that photocatalytic paint should not

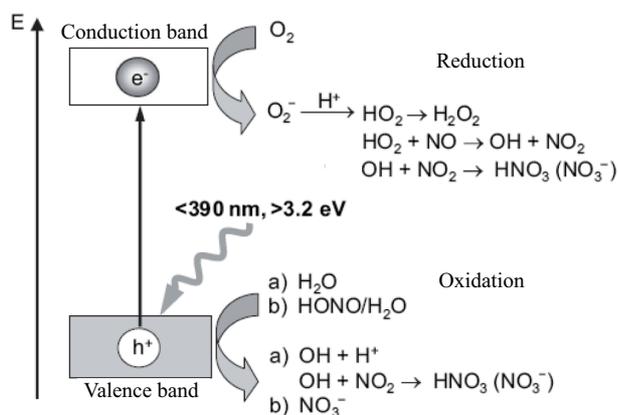
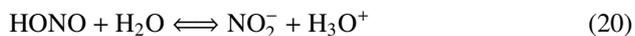


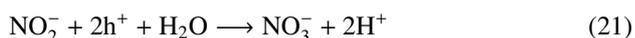
Fig. 3 Postulated mechanism for the photocatalytic reaction of NO, NO₂, and HONO on TiO₂-containing photoactive paint surfaces (Laufs et al., 2010).

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).

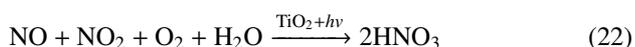
Not gas phase HONO but the solution of NO₂⁻ in a film of adsorbed water was proposed:



Soluble NO₂⁻ is further oxidized by electron holes to NO₃⁻:



All studied nitrogen species (NO, NO₂, HONO) are photocatalytically oxidized leading to NO₃⁻, while O₂ is photochemically reduced. The near unity yield of NO₃⁻ 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 TiO₂ (Gustafsson et al., 2006), TiO₂/SiO₂ 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 TiO₂ 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_x.

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 TiO₂ (Ndour et al., 2008). Although the amounts of TiO₂

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 NO₂ 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 HNO₃/nitrate and photoreaction of NO₂ on TiO₂-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_x. Therefore, further kinetic studies under atmospherically relevant conditions are necessary to better understand the photochemistry of NO_y in the atmosphere.

2 Photochemical reactions on organic aerosol

The heterogeneous reaction of NO₂ 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 NO₂ to HONO has been extensively studied in the laboratory for a broad range of NO₂ 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 NO₂, the reported uptake coefficients vary over 7 orders of magnitude, from 10⁻¹ to 10⁻⁸, 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 NO₂ 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 NO₂ and solid pyrene/KNO₂ 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 NO₂ to HONO and NO, with yields of ca. 15% and ca. 30%, respectively.

The reactivity and HONO yields for the reaction of NO₂ 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 10⁻⁶ 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 NO₂ 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 NO₂ 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 NO₂ 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 ₂] by dark reaction ^b (%)	Yield of HONO per reacted NO ₂ in dark reaction (%)	Removal of initial [NO ₂] by light reaction ^{cd} (%)	Yield of HONO per reacted NO ₂ 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 ^e	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 ^a	4	4	36/36	61/70
Sodium 4-benzoylbenzoate (1 mg)				
Syringic acid (0.5 mg)				
External mixture ^a	2	n.a.	42/38	91/90
Sodium 4-benzoylbenzoate (1 mg)				
3,4-Dihydroxyphenylacetic acid (1 mg)				
External mixture ^a	14	n.a.	66/58	93/101
Sodium 4-benzoylbenzoate (1 mg)				
Potassium iodide (1 mg)				
External mixture ^a	2	n.a.	6/9	57/67
Perylene (0.5 mg)				
3,4-Dihydroxyphenylacetic acid (1 mg)				
External mixture ^a	20	> 80	7/10	n.a.
Perylene (0.5 mg)				
Potassium iodide (1 mg)				
Internal mixture ^a	16	n.a.	52/63	90/93
4-Benzoylbenzoic acid (1 mg)				
3,4-Dihydroxyphenylacetic acid (0.5 mg)				
Internal mixture ^a	7	n.a.	47/58	95/97
4-Benzoylbenzoic acid (1 mg)				
3,4-Dihydroxyphenylacetic acid (1 mg)				

^a 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.

^b The removal of NO₂ due to the dark reaction was measured by exposing the coated wall reactor to the NO₂-mixture and measuring the decrease of the NO₂ concentration.

^c The removal of NO₂ due to the light reaction was measured by illuminating the NO₂-mixture flowing through the coated wall reactor and comparing the NO₂ concentration before and during the irradiation.

^d Values after 5 and 10 min of irradiation, respectively.

^e Values after 5, 10 and 25 min of irradiation, respectively.

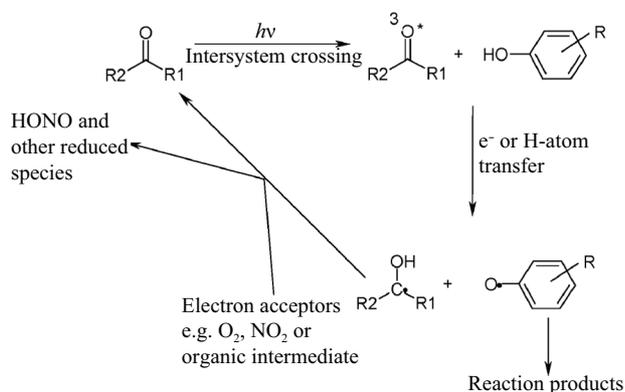


Fig. 4 Proposed reaction mechanism for the photoreduction of NO₂ to HONO in the presence of 4-BBA (absorbing photosensitizer) and a substituted phenol (electron donor) (George et al., 2005).

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 NO₂.

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 NO₂ 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 NO₂ to form HONO.



where, A^{red} is photo-produced reductive centers, X^{ox} 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 NO₂ 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 NO₂ 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 NO₂ 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 HNO₃, by photocatalytic reaction of NO₂ on TiO₂ or TiO₂-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.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21207145, 20937004) and the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB05050600). This work was also financially supported by the Special Co-construction Project of the Beijing Municipal Commission of Education.

References

- Acker K, Möller D, Wieprecht W, Meixner F X, Bohn B, Gilge S et al., 2006. Strong daytime production of OH from HNO₂ at a rural mountain site. *Geophysical Research Letters*, 33(2): L02809.
- Ackerman A S, Toon O B, Stevens D E, Heymsfield A J, Ramanathan V, Welton E J, 2000. Reduction of tropical cloudiness by soot. *Science*, 288(5468): 1042–1047.
- Al-Abadleh H A, Grassian V H, 2000. Heterogeneous reaction of NO₂ on hexane soot: A Knudsen cell and FT-IR study. *Journal of Physical Chemistry A*, 104(51): 11926–11933.
- Alicke B, Geyer A, Hofzumahaus A, Holland F, Konrad S, Pätz H W et al., 2003. OH formation by HONO photolysis during the BERLIOZ experiment. *Journal of Geophysical Research*, 108(D4): 8247–8249.
- Alicke B, Platt U, Stutz J, 2002. Impact of nitrous acid photolysis on the total hydroxyl radical budget during the limitation of oxidant production/pianura padana produzione di ozono study in Milan. *Journal of Geophysical Research*, 107(D22): 8196–8204.
- Ammann M, Kalberer M, Jost D T, Tobler L, Rössler E, Piguet D et al., 1998. Heterogeneous production of nitrous acid on soot in polluted air masses. *Nature*, 395(6698): 157–160.
- Ammar R, Monge M E, George C, D'Anna B, 2010. Photoenhanced NO₂ loss on simulated urban grime. *Chemphyschem*, 11(18): 3956–3961.
- Arens F, Gutzwiller L, Baltensperger U, Gäggeler H W, Ammann M, 2001. Heterogeneous reaction of NO₂ on diesel soot particles. *Environmental Science and Technology*, 35(11): 2191–2199.
- Aubin D G, Abbatt J P D, 2007. Interaction of NO₂ with hydrocarbon soot: Focus on HONO yield, surface modification, and mechanism. *Journal of Physical Chemistry A*, 111(28): 6263–6273.
- Aumont B, Chervier F, Laval S, 2003. Contribution of HONO sources to the NO_x/HO_x/O₃ chemistry in the polluted boundary layer. *Atmospheric Environment*, 37(4): 487–498.
- Aumont B, Madronich S, Ammann M, Kalberer M, Baltensperger U, Hauglustaine D et al., 1999. On the NO₂ + soot reaction in the atmosphere. *Journal of Geophysical Research*, 104(D1): 1729–1736.
- Bartels-Rausch T, Brigante M, Elshorbany Y F, Ammann M, D'Anna B, George C et al., 2010. Humic acid in ice: Photoenhanced conversion of nitrogen dioxide into nitrous acid. *Atmospheric Environment*, 44(40): 5443–5450.
- Batjes N H, 1996. Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science*, 47(2): 151–163.
- Beaumont S K, Gustafsson R J, Lambert R M, 2009. Heterogeneous photochemistry relevant to the troposphere: H₂O₂ production during the photochemical reduction of NO₂ to HONO on UV-illuminated TiO₂ surfaces. *Chemphyschem*, 10(2): 331–333.
- Brigante M, Cazoir D, D'Anna B, George C, Donaldson D J, 2008. Photoenhanced uptake of NO₂ by pyrene solid films. *Journal of Physical Chemistry A*, 112(39): 9503–9508.
- Bröske R, Kleffmann J, Wiesen P, 2003. Heterogeneous conversion of NO₂ on secondary organic aerosol surfaces: A possible source of nitrous acid (HONO) in the atmosphere? *Atmospheric Chemistry and Physics*, 3(3): 469–474.
- Chameides W L, Bergin M, 2002. Climate change – Soot takes center stage. *Science*, 297(5590): 2214–2215.
- Chen H H, Navea J G, Young M A, Grassian V H, 2011. Heterogeneous photochemistry of trace atmospheric gases with components of mineral dust aerosol. *Journal of Physical Chemistry A*, 115(4): 490–499.
- Dibb J E, Arsenault M, Peterson M C, Honrath R E, 2002. Fast nitrogen oxide photochemistry in Summit, Greenland snow. *Atmospheric Environment*, 36(15–16): 2501–2511.
- Dibb J E, Gregory H L, Slusher D L, Tanner D J, 2004. Soluble reactive nitrogen oxides at South Pole during ISCAT 2000. *Atmospheric Environment*, 38(32): 5399–5409.
- Dubowski Y, Sumner A L, Menke E J, Gaspar D J, Newberg J T, Hoffman R C et al., 2004. Interactions of gaseous nitric acid with surfaces of environmental interest. *Physical Chemistry Chemical Physics*, 6(14): 3879–3888.
- Escribano R, Couceiro M, Gómez P C, Carrasco E, Moreno M A, Herrero V J, 2003. The nitric acid hydrates: *Ab initio* molecular study, and RAIR spectra of the solids. *Journal of Physical Chemistry A*, 107(5): 651–661.
- Fernández D, Botella V, Herrero V J, Escribano R, 2003. A theoretical study of the structure and spectra of nitric acid hydrates crystals. *Journal of Physical Chemistry B*, 107(38): 10608–10614.
- Finlayson-Pitts B J, Wingen L M, Sumner A L, Syomin D, Ramazan K A, 2003. The heterogeneous hydrolysis of NO₂ in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism. *Physical Chemistry Chemical Physics*, 5(2): 223–242.
- Gelencsér A, Hoffer A, Kiss G, Tombác E, Kurdi R, Bencze L, 2003. In-situ formation of light-absorbing organic matter in cloud water. *Journal of Atmospheric Chemistry*, 45(1): 25–33.
- George C, Strekowski R S, Kleffmann J, Stemmler K, Ammann M, 2005. Photoenhanced uptake of gaseous NO₂ on solid-organic compounds: a photochemical source of HONO? *Faraday Discussions*, 130: 195–210.
- Gerecke A, Thielmann A, Gutzwiller L, Rossi M J, 1998. The chemical kinetics of HONO formation resulting from heterogeneous interaction of NO₂ with flame soot. *Geophysical Research Letters*, 25(13): 2453–2456.
- Goodman A L, Underwood G M, Grassian V H, 1999. Heterogeneous reaction of NO₂: Characterization of gas-phase and adsorbed products from the reaction, 2NO₂(g)+H₂O(a)→HONO(g)+HNO₃(a) on hydrated silica particles. *Journal of Physical Chemistry A*, 103(36): 7217–

- 7223.
- Gustafsson R J, Orlov A, Griffiths P T, Cox R A, Lambert R M, 2006. Reduction of NO₂ to nitrous acid on illuminated titanium dioxide aerosol surfaces: implications for photocatalysis and atmospheric chemistry. *Chemical Communications*, (37): 3936–3938.
- Harrison R M, Peak J D, Collins G M, 1996. Tropospheric cycle of nitrous acid. *Journal of Geophysical Research*, 101(D9): 14429–14439.
- Honrath R E, Lu Y, Peterson M C, Dibb J E, Arsenault M A, Cullen N J et al., 2002. Vertical fluxes of NO_x, HONO, and HNO₂ above the snowpack at Summit, Greenland. *Atmospheric Environment*, 36(15): 2629–2640.
- Jacobson M Z, 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, 409(6821): 695–697.
- Jang M S, Czoschke N M, Lee S, Kamens R M, 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. *Science*, 298(5594): 814–817.
- Janzen H H, 2004. Carbon cycling in earth systems – A soil science perspective. *Agriculture, Ecosystems & Environment*, 104(3): 399–417.
- Kalberer M, Ammann M, Arens F, Gäggeler H W, Baltensperger U, 1999. Heterogeneous formation of nitrous acid (HONO) on soot aerosol particles. *Journal of Geophysical Research*, 104(D11): 13825–13832.
- Kalberer M, Paulsen D, Sax M, Steinbacher M, Dommen J, Prevot A S H et al., 2004. Identification of polymers as major components of atmospheric organic aerosols. *Science*, 303(5664): 1659–1662.
- Khalizov A F, Cruz-Quinones M, Zhang R Y, 2010. Heterogeneous reaction of NO₂ on fresh and coated soot surfaces. *Journal of Physical Chemistry A*, 114(28): 7516–7524.
- Kleffmann J, 2007. Daytime sources of nitrous acid (HONO) in the atmospheric boundary layer. *Chemphyschem*, 8(8): 1137–1144.
- Kleffmann J, Becker K H, Lackhoff M, Wiesen P, 1999. Heterogeneous conversion of NO₂ on carbonaceous surfaces. *Physical Chemistry Chemical Physics*, 1(24): 5443–5450.
- Kleffmann J, Gavriloaiei T, Hofzumahaus A, Holland F, Koppmann R, Rupp L et al., 2005. Daytime formation of nitrous acid: A major source of OH radicals in a forest. *Geophysical Research Letters*, 32(5): L05818.
- Kleffmann J, Kurtenbach R, Lörzer J, Wiesen P, Kalthoff N, Vogel B et al., 2003. Measured and simulated vertical profiles of nitrous acid – Part I: Field measurements. *Atmospheric Environment*, 37(21): 2949–2955.
- Kleffmann J, Wiesen P, 2005. Heterogeneous conversion of NO₂ and NO on HNO₃ treated soot surfaces: atmospheric implications. *Atmospheric Chemistry and Physics*, 5(1): 77–83.
- Langridge J M, Gustafsson R J, Griffiths P T, Cox R A, Lambert R M, Jones R L, 2009. Solar driven nitrous acid formation on building material surfaces containing titanium dioxide: A concern for air quality in urban areas? *Atmospheric Environment*, 43(32): 5128–5131.
- Laufs S, Burgeth G, Duttlinger W, Kurtenbach R, Maban M, Thomas C et al., 2010. Conversion of nitrogen oxides on commercial photocatalytic dispersion paints. *Atmospheric Environment*, 44(19): 2341–2349.
- Lelièvre S, Bedjanian Y, Laverdet G, Le Bras G, 2004. Heterogeneous reaction of NO₂ with hydrocarbon flame soot. *Journal of Physical Chemistry A*, 108(49): 10807–10817.
- Liu C, Ma Q X, Liu Y C, Ma J Z, He H, 2012. Synergistic reaction between SO₂ and NO₂ on mineral oxides: a potential formation pathway of sulfate aerosol. *Physical Chemistry Chemical Physics*, 14(5): 1668–1676.
- Ma J Z, Liu Y C, Ma Q X, Liu C, He H, 2011a. Atmospheric heterogeneous reactions and their environmental effects. *Environmental Chemistry*, 30(1): 97–118.
- Ma J Z, Liu Y C, He H, 2011b. Heterogeneous reactions between NO₂ and anthracene adsorbed on SiO₂ and MgO. *Atmospheric Environment*, 45(4): 917–924.
- McCurdy P R, Hess W P, Xantheas S S, 2002. Nitric acid-water complexes: Theoretical calculations and comparison to experiment. *Journal of Physical Chemistry A*, 106(33): 7628–7635.
- Monge M E, D'Anna B, George C, 2010a. Nitrogen dioxide removal and nitrous acid formation on titanium oxide surfaces – an air quality remediation process? *Physical Chemistry Chemical Physics*, 12(31): 8992–8999.
- Monge M E, D'Anna B, Mazri L, Giroir-Fendler A, Ammann M, Donaldson D J et al., 2010b. Light changes the atmospheric reactivity of soot. *Proceedings of the National Academy of Sciences of the United States of America*, 107(15): 6605–6609.
- Ndour M, D'Anna B, George C, Ka O, Balkanski Y, Kleffmann J et al., 2008. Photoenhanced uptake of NO₂ on mineral dust: Laboratory experiments and model simulations. *Geophysical Research Letters*, 35(5): L05812.
- Pitts Jr J N, Grosjean D, Van Cauwenberghe K, Schmid J P, Fitz D R, 1978. Photooxidation of aliphatic amines under simulated atmospheric conditions: formation of nitrosamines, nitramines, amides, and photochemical oxidant. *Environmental Science and Technology*, 12(8): 946–953.
- Ramazan K A, Syomin D, Finlayson-Pitts B J, 2004. The photochemical production of HONO during the heterogeneous hydrolysis of NO₂. *Physical Chemistry Chemical Physics*, 6(14): 3836–3843.
- Ramazan K A, Wingen L M, Miller Y, Chaban G M, Gerber R B, Xantheas S S et al., 2006. New experimental and theoretical approach to the heterogeneous hydrolysis of NO₂: Key role of molecular nitric acid and its complexes. *Journal of Physical Chemistry A*, 110(21): 6886–6897.
- Ren X R, Harder H, Martinez M, Leshner R L, Olinger A, Simpas J B et al., 2003. OH and HO₂ chemistry in the urban atmosphere of New York City. *Atmospheric Environment*, 37(26): 3639–3651.
- Rohrer F, Bohn B, Brauers T, Brüning D, Johnen F J, Wahner A et al., 2005. Characterisation of the photolytic HONO source in the atmosphere simulation chamber SAPHIR. *Atmospheric Chemistry and Physics*, 5(8): 2189–2201.
- Rubasinghe G, Grassian V H, 2009. Photochemistry of adsorbed nitrate on aluminum oxide particle surfaces. *Journal of Physical Chemistry A*, 113(27): 7818–7825.
- Salgado M S, Rossi M J, 2002. Flame soot generated under controlled combustion conditions: Heterogeneous reaction of NO₂ on hexane soot. *International Journal of Chemical Kinetics*, 34(11): 620–631.
- Sarwar G, Roselle S J, Mathur R, Appel W, Dennis R L, Vogel

- B, 2008. A comparison of CMAQ HONO predictions with observations from the Northeast Oxidant and Particle Study. *Atmospheric Environment*, 42(23): 5760–5770.
- Schuttlefield J, Rubasinghege G, El-Maazawi M, Bone J, Grassian V H, 2008. Photochemistry of adsorbed nitrate. *Journal of the American Chemical Society*, 130(37): 12210–12211.
- Stadler D, Rossi M J, 2000. The reactivity of NO₂ and HONO on flame soot at ambient temperature: The influence of combustion conditions. *Physical Chemistry Chemical Physics*, 2(23): 5420–5429.
- Staffelbach T, Neftel A, Horowitz L W, 1997. Photochemical oxidant formation over southern Switzerland. 2. Model results. *Journal of Geophysical Research*, 102(D19): 23363–23373.
- Staikova M, Donaldson D J, 2001. *Ab initio* investigation of water complexes of some atmospherically important acids: HONO, HNO₂ and HO₂NO₂. *Physical Chemistry Chemical Physics*, 3(11): 1999–2006.
- Stemmler K, Ammann M, Donders C, Kleffmann J, George C, 2006. Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. *Nature*, 440(7081): 195–198.
- Stemmler K, Ndour M, Elshorbany Y, Kleffmann J, D'Anna B, George C et al., 2007. Light induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol. *Atmospheric Chemistry and Physics*, 7(16): 4237–4248.
- Su H, Cheng Y F, Oswald R, Behrendt T, Trebs I, Meixner F X et al., 2011. Soil nitrite as a source of atmospheric HONO and OH radicals. *Science*, 333(6049): 1616–1618.
- Swift R S, 2001. Sequestration of carbon by soil. *Soil Science*, 166(11): 858–871.
- Syomin D A, Finlayson-Pitts B J, 2003. HONO decomposition on borosilicate glass surfaces: implications for environmental chamber studies and field experiments. *Physical Chemistry Chemical Physics*, 5(23): 5236–5242.
- Usher C R, Michel A E, Grassian V H, 2003. Reactions on mineral dust. *Chemical Reviews*, 103(12): 4883–4940.
- Vogel B, Vogel H, Kleffmann J, Kurtenbach R, 2003. Measured and simulated vertical profiles of nitrous acid—Part II. Model simulations and indications for a photolytic source. *Atmospheric Environment*, 37(21): 2957–2966.
- Zhang R Y, Khalizov A F, Pagels J, Zhang D, Xue H X, McMurry P H, 2008. Variability in morphology, hygroscopicity, and optical properties of soot aerosols during atmospheric processing. *Proceedings of the National Academy of Sciences of the United States of America*, 105(30): 10291–10296.
- Zhou X L, Beine H J, Honrath R E, Fuentes J D, Simpson W, Shepson P B et al., 2001. Snowpack photochemical production of HONO: a major source of OH in the Arctic boundary layer in springtime. *Geophysical Research Letters*, 28(21): 4087–4090.
- Zhou X L, Civerolo K, Dai H P, Huang G, Schwab J, Demerjian K, 2002a. Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York State. *Journal of Geophysical Research*, 107(D21): 4590–4600.
- Zhou X L, Gao H L, He Y, Huang G, Bertman S B, Civerolo K et al., 2003. Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric implications. *Geophysical Research Letters*, 30(23): 2217–2220.
- Zhou X L, He Y, Huang G, Thornberry T D, Carroll M A, Bertman S B, 2002b. Photochemical production of nitrous acid on glass sample manifold surface. *Geophysical Research Letters*, 29(14): 1681–1684.
- Zhou X L, Zhang N, TerAvest M, Tang D, Hou J, Bertman S et al., 2011. Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid. *Nature Geoscience*, 4(7): 440–443.