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Key role of pH in the photochemical conversion of NO_2 to HONO on humic acid

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HIGHLIGHTS

- The γ of NO_2 on HA almost remained unchanged with increasing the pH.
- There was a negatively linear dependence trend of the HONO yield on the pH.
- The contents of carboxyl and phenol in HA significantly decreased with the pH.
- Key role of pH in the HONO yield was related to its effects on the HA composition.

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ABSTRACT

The heterogeneous photochemical reactions of NO_2 with humic acid (HA) were performed using a flow tube reactor coupled to a NO_x analyzer. The effects of the pH on the uptake coefficient (γ) of NO_2 and HONO and NO yields were investigated in detail. With increasing the pH in the range of 2–12, γ was almost constant with an average value of $(4.21 \pm 0.46) \times 10^{-6}$, whereas the HONO yield and NO yield linearly decreased from $(81.07 \pm 4.07)\%$ and $(10.35 \pm 3.86)\%$ to $(13.87 \pm 9.15)\%$ and $(1.51 \pm 0.94)\%$, respectively. According to the characterization of HA compositions and possible reaction paths, it can be concluded that the pH may influence the transfer of protons and the equilibrium of HONO with NO_2^- by varying the contents of carboxyl and phenol groups in HA, which should primarily contribute to the change in the HONO yield with the pH.

1. Introduction

HONO has attracted extensive attention because of its importance to produce OH radical by photolysis. As a significant oxidant in the atmosphere, OH radical can react with most of pollutants emitted by natural and anthropogenic activities. The contribution ratio of HONO to the initial sources of OH radical may account for 30–60% (Ren et al., 2003; Su et al., 2008). However, the HONO sources during the daytime still remain unclear. Recently, it was found that the heterogeneous photochemical reactions of NO_2 with soot and mineral dust containing TiO_2 can produce more HONO compared with that in the dark (Gustafsson et al., 2006; Monge et al., 2010a, 2010b; Ndour et al., 2008). Photoenhanced conversion of NO_2 to HONO on organic compounds such as pyrene, fluoranthene, benzophenone-catechol, and polyphenolic species has been also reported (Ammar et al., 2010; Brigante et al., 2008; Cazoir et al., 2014; George et al., 2005; Sosedova et al., 2011). In addition, HONO is also an important pollutant within indoor environments and its photolysis makes a great contribution to indoor OH radical (Gligorovski and Weschler, 2013). A HONO source induced by the reactions of NO_2 with indoor paint surfaces has been presented under irradiation (Bartolomei et al., 2014). These results indicate that heterogeneous photochemical processes of NO_2 on aerosols may become an important HOHO source.

Humic substances are ubiquitous in the terrestrial, aquatic and atmospheric system (Amir et al., 2004; Dmitrieva et al., 2015; Gieguzynska et al., 2009). They contain a high content of aromatic moieties with many oxygenated functional groups such as C-O, C=O, OH and COOH (Carletti et al., 2010). The biomass burning tracers and secondary species, which correspondingly accounted for 8.5% and 10.2% of PM2.5 mass (Kuang et al., 2015), were associated with humic like substances. Due to aromatic moieties acting as the light absorbers and phenolic functionalities as the electron

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donors, humic substances can enhance chemical transformation processes under irradiation (D'Anna et al., 2009).

Humic acid (HA) is the important components of humic substances. It was reported that ultraviolet or visible light can significantly promote the heterogeneous conversion of NO_2 to HONO on HA, where the HONO yield reached 80% (Stemmler et al., 2006, 2007). The presence of HA resulted in the formation of more HONO when NO_2 contacted with ice and snow under irradiation (Bartels-Rausch et al., 2010; Beine et al., 2008). Thus, the heterogeneous photochemical uptake of NO_2 on HA may contribute to the HONO source during the daytime. The photochemical conversion ratio of NO_2 to HONO on HA strongly depended on various environmental conditions such as irradiation intensity, relative humidity, NO_2 concentration, and pH.

In particular, the pH was a critical factor for HONO formation during the photochemical reaction of NO_2 with HA (Bartels-Rausch et al., 2010; Stemmler et al., 2007). Upon irradiation, NO_2 uptake occurred instantaneously, and its loss amounts were almost constant in the range of pH = 4.4–10.3 (Stemmler et al., 2007). Nevertheless, HONO formation had a larger constraint with increasing the pH (Stemmler et al., 2007). An analogous effect of the pH on HONO formation was also observed for the reaction of NO_2 with ice containing HA under visible light (Bartels-Rausch et al., 2010). It is speculated that the dependence of HONO formation on the pH may be related to the protonation equilibrium or structural changes of HA. More efforts are still needed to further explain how and why the pH influences HONO formation in the uptake process of NO_2 on HA under irradiation.

In this work, the effects of the pH on the heterogeneous photochemical conversion of NO_2 to HONO on HA were investigated using a flow tube reactor coupled to a NO_x analyzer at ambient pressure. The light absorption ability of fresh HA at different pH was analyzed by the UV–visible diffuse reflectance spectrum (UV–vis DRS). The functional groups of fresh HA and HA reacted by NO_2 were examined through a Fourier transform infrared (FTIR) spectroscopy. A series of possible reaction paths were discussed to explain the important role of the pH in the HONO formation from the reaction of NO_2 with HA under irradiation.

2. Experimental section

2.1. Materials

HA sodium salt (Sigma-Aldrich) was dissolved in the deionized water, which was used to prepare the HA coating. The pH of HA solution was adjusted to the desired value by HCl and NaOH. These samples were directly used without further purification or isolation. The inner surface of a quartz tube (20 cm length, 1.0 cm inner diameter) was carefully coated with 1.0 mL HA solution (1.0 mg/mL). The HA coating was produced by drying HA solution in a N_2 stream at room temperature and was uniform on the whole. NO_2 standard gas (50 ppm in N_2, Dalian Special Gases Co., LTD) and high purity N_2 (99.99%, Shenyang Gases Co., LTD) were used as received.

2.2. Flow tube reactor

The heterogeneous photochemical experiments of NO_2 with HA were performed in a horizontal cylindrical coated-wall flow tube reactor (34 cm length, 1.6 cm inner diameter), which has been described in detail elsewhere (Han et al., 2013; Liu et al., 2015). The temperature was maintained at 298 K by circulating temperature-controlled water through the outer jacket of flow tube reactor. With high purity N_2 as carrier gas, NO_2 was introduced into the reactor by a movable injector and its concentration was 30 ppb. The relative humidity was maintained at 22% by controlling the ratio of dry N_2 to humid N_2 using mass flow meters. The value of relative humidity was measured by a hygrometer (Center 314). Total gas flow rate into the reactor was 900 mL min^{-1}, ensuring a laminar regime at ambient pressure. The xenon lamp was used to simulate sunlight in the photochemical studies, because the shape of the spectrum of the xenon lamp is similar to that of the solar spectrum (Halle and Richard, 2006; Murphy et al., 2006; Yager and Yue, 1988; Ye et al., 2016). Two xenon lamps (250 W) were installed above and under the reactor, respectively. The irradiation intensity on the HA surface was 194.5 W/m^2, which was within the typical solar irradiance range (0–350 W/m^2) over the earth surface (Pinker and Laszlo, 1992; Bishop and Rossow, 1991). It has been confirmed that NO_2 photolysis, NO_2 uptake, and HONO and NO formation on the quartz tube were negligible in the blank experiments. In addition, to collect and characterize HA reacted by NO_2, HA can be coated on a small quartz plate instead of a quartz tube. After the reaction with NO_2 under the conditions mentioned above, the quartz plate coated with HA was taken out from the flow tube reactor, and then HA was scraped carefully to achieve the collection.

2.3. Gases measurements

A chemiluminescence NO_x analyzer (Thermo 42i) was employed to detect the NO_2 and NO concentrations as a function of the gas-surface contact time. Because of HONO detected as NO_2 by the analyzer, a quartz tube (10 cm × 0.6 cm inner diameter) filled with Na_2CO_3 was introduced to trap the formed HONO between the exit of the flow tube reactor and the detector. NO and NO_2 together with HONO were detected using a bypass tube while only NO and NO_2 were measured using this quartz tube. Therefore, the HONO concentration can be indirectly measured as the difference between the detected NO_2 signals with and without the Na_2CO_3 tube. The HONO detection technique has been proved to be valid and widely used to measure the HONO concentration (Ammar et al., 2010; Brigante et al., 2008; Cazoir et al., 2014; Monge et al., 2010b). A new Na_2CO_3 tube was installed before each uptake experiment to avoid the saturation effects. The small amount of NO_2 trapped by the Na_2CO_3 tube has been corrected in the calculation of the uptake coefficient and product yield.

2.4. Uptake coefficient

According to Eq (1), the uptake coefficient of NO_2 was proportional to the measured first-order rate constant (k_{obs}) from the uptake curves when the Na_2CO_3 tube was used in the sampling line.

$$\frac{\ln(C_0/C_t)}{t} = k_{obs} = \frac{\gamma\langle c\rangle}{2r_{tube}} \tag{1}$$

where C_0 and C_t are the NO_2 concentration at time $t = 0$ and t, respectively; γ, r_{tube}, and $\langle c\rangle$ are the geometric uptake coefficient, the flow tube radius, and the average molecular velocity of NO_2, respectively. k_{obs} was determined by pulling the injector back to the end of the sample tube. The geometric inner surface area of the whole sample tube was used to calculate γ. Cooney-Kim-Davis (CKD) method was used to correct γ since a radial concentration gradient may cause diffusion limitations (Cooney et al., 1974; Murphy and Fahey, 1987). γ was calculated using the average signal within the first 1.0 h.

2.5. UV–vis DRS and FTIR spectra analysis

The UV–vis DRS was recorded to measure light absorption abilities of HA at different pH using a UV–visible spectrophotometer (SHIMADZU UV-2550) with $BaSO_4$ as the reference. To