Significant influences of TiO₂ crystal structures on NO₂ and HONO emissions from the nitrates photolysis

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The emissions of NO₂ and HONO from the KNO₃ photolysis in the presence of TiO₂ were measured using a round-shape reactor coupled to a NO₂ analyzer. TiO₂ played important roles in the emission flux density of NO₂ (RNO₂) and HONO (RHONO), depending on crystal structures and mass ratios of TiO₂. RNO₂ and RHONO significantly decreased with increasing the rutile and anatase mass ratios from 0 to 8 and 0.5 wt.%, respectively. Nevertheless, with further increasing the anatase mass ratio to 8 wt.%, there was an increase in RNO₂ and RHONO. RNO₂ on KNO₃/TiO₂/SiO₂ had positive correlation with the KNO₃ mass (1–20 wt.%), irradiation intensity (80–400 W/m²) and temperature (278–308 K), while it had the maximum value at the relative humidity (RH) of 55%. RHONO on KNO₃/TiO₂/SiO₂ slightly varied with the KNO₃ mass and temperature, whereas it increased with the irradiation intensity and RH. In addition, the mechanism for NO₂ and HONO emissions from the nitrates photolysis and atmospheric implications were discussed.

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Introduction

Nitrates are one of the main components in atmospheric aerosols, and they account for 3%–30% and 1%–24% of fine particulate matter (PM₂.5, aerodynamic particle size <2.5 μm) mass in urban and rural regions (Reuvela et al., 2012; Wen et al., 2015), respectively. Nitrates have significant environmental and health effects. For example, nitrates can act as ice nuclei (IN) and cloud condensation nuclei (CCN) (Ishizaka and Adhikari, 2003), influencing the cloud formation and the precipitation distribution. Nitrates directly influence the earth’s radiation balance by absorbing and scattering solar radiation (Laskin et al., 2019). It has been shown that respiratory diseases, circulatory diseases and malignant tumours correlate with nitrates in the atmospheric aerosols, which causes serious harm to human health (Tang et al., 2017). In addition, nitrates and HNO₃ are considered to be sinks for atmospheric nitrogen oxides (NOx, i.e., NO and NO₂) (Ostaszewski et al., 2018; Zhou et al., 2003). Nitrates can be recycled back to the atmosphere in the forms of NOx and nitrous acid (HONO) by the renoxification process (Baergen and Donaldson, 2013, 2016; Chen et al., 2011; Handley et al., 2007; Saliba et al., 2001; Ye et al., 2016; Zhou et al., 2003; Zhu et al., 2010).

Several studies have investigated the renoxification process of nitrates/HNO₃ (Blaszczak-Boxe and Saiz-Lopez, 2018; Kleffmann et al., 2004; McFall et al., 2018; Morenz et al., 2016; Rivera-Figueroa et al., 2003; Ye et al., 2016a; Zhou et al., 2003, 2011). For instance, the heterogeneous reaction of NO with HONO generated HONO and NO₂ on silica (Rivera-
Figueroa et al., 2003) and glass surfaces (Kleffmann et al., 2004). In particular, NO₂ and HONO could be produced by the photolysis of nitrates/HNO₃ adsorbed on various surfaces, including ice (Blaszczyk-Boxe and Saiz-Lopez, 2018; McFall et al., 2018), snow (Blaszczyk-Boxe and Saiz-Lopez, 2018; Morenz et al., 2016), plant leaves (Zhou et al., 2003, 2011), metal sheets and construction materials (Ye et al., 2016a). The HONO photolysis is an important source of hydroxyl radicals in the atmosphere and indoor air environments (Gomez Alvarez et al., 2013; Liu et al., 2019b; Zhou et al., 2018). Hydroxyl radicals can participate in the atmospheric oxidation cycles and react with most pollutants. It was reported that 30%–60% of hydroxyl radicals in the atmosphere originate from the photolysis of HONO (Ren et al., 2003; Su et al., 2008).

At present, the contribution of nitrates photolysis to HONO still remained uncertain. A very low HONO formation was observed during the photolysis of HNO₃ adsorbed on clean quartz glass surfaces (Laufs and Kleffmann, 2016), whereas the photolysis of nitrates or nitric acids was also found to be an important daytime source of HONO in the lower atmosphere (Kleffmann, 2007; Ye et al., 2016a, 2017; Zhou et al., 2011). This uncertainty may be ascribed to the mixed states of nitrates, which generally involved with various organic and inorganic substances in the atmosphere. It has been confirmed that humic acids (Yang et al., 2018) and aluminum oxides (Rubasinghe and Grassian, 2009) enhanced the photolysis of nitrates to generate HONO and NO₂.

TiO₂ is one of important mineral oxides, and its content in atmospheric aerosols varied in the range of 0.1%–10% (Hanisch and Crowley, 2003; Ndour et al., 2009a). As an effective photocatalyst (El Zein and Bedjianian, 2012b; Ndour et al., 2008, 2009a, 2009b), TiO₂ plays significant roles in atmospheric chemistry. The conversion of NO₂ to HONO (Bedjianian and El Zein, 2012; Gandolfó et al., 2015, 2017; Gustaffson et al., 2006) and the decomposition of O₃ (Nicolas et al., 2009) on TiO₂ could be greatly enhanced under irradiation. Few studies have investigated the influences of TiO₂ on the nitrates photolysis (Ndour et al., 2009a). It was observed that TiO₂ promoted photochemical conversion of nitrates to NO and NO₂ (Ndour et al., 2009a), indicating that photoactive oxides in mineral dust were efficient for the nitrates photochemistry (Gankanda and Grassian, 2014). It should be pointed out that TiO₂ has three polymorphs including rutile, anatase and brookite (Etacheri et al., 2015; Catal et al., 2020), whereas their effects on the nitrates photolysis remain unexplored. In addition, the nitrates photolysis were carried out under ultraviolet light in previous studies (Ndour et al., 2009a). To better obtain practical data, the nitrates photolysis should be further measured under real or simulated sunlight with a continuous wavelength range.

With a round-shape reactor coupled to a NO₂ analyzer, the roles of TiO₂ crystal structures in the photolysis of KNO₃ to generate NO₂ and HONO were investigated under simulated sunlight. The emission flux density of NO₂ and HONO on KNO₃/TiO₂/SiO₂ were measured under various environmental conditions, such as KNO₃ mass, irradiation intensity, relative humidity (RH) and temperature. A series of possible reaction pathways were proposed to explain the NO₂ and HONO generation from photochemical process of KNO₃/TiO₂/SiO₂. Finally, the nitrates photolysis in the presence of TiO₂ for atmospheric implications were discussed.

1. Materials and methods

1.1. Materials

KNO₃ (Sinopharm Chemical Reagent Co., Ltd), TiO₂ (Macklin Biochemical Co., Ltd) and SiO₂ (Sinopharm Chemical Reagent Co., Ltd) with a total mass of 2.0 g were used to prepare the sample coating. KNO₃ (1–20 wt.%, mass ratio), TiO₂ (0–8 wt.%, mass ratio) and SiO₂ were mixed in 8.0 mL of absolute ethanol solution. SiO₂ mass was determined after setting the desired mass ratio of KNO₃ and TiO₂. A stainless steel sample dish (7.0 cm diameter) was coated with the mixture above. Then, the uniform coating was prepared by drying the mixture overnight in an oven at 373 K. NO₂ standard gas (50 ppmV in N₂, Dalian Special gasses Co., LTD) and high purity N₂ and O₂ (99.99 vol.%, Shenyang gasses Co., LTD) were used.

1.2. Round-shape reactor

A round-shape reactor with the volume of 50.2 cm³ (1.0 cm height, 8.0 cm diameter) was used to investigate the photolysis of KNO₃, and it was fully made of stainless steel material except for the quartz window, as shown in Appendix A Fig. S1. A xenon lamp (500 W) with a continuous light emission in the range of 300–700 nm was used to simulate sunlight. As shown in the Appendix A Fig. S2, the spectrum irradiance of the xenon lamp was measured by a calibrated spectroradiometer (ULSZ2048CL-EVO, Avantes, Netherlands), and it was similar to the spectrum irradiance of the solar (Halle and Richard, 2006; Murphy et al., 2006; Ye et al., 2016b). It should be noted that there were very few wavelengths below 300 nm for the xenon lamp, which was almost non-existent for the solar and may have effects on the nitrates photolysis. The irradiation intensity (80–400 W/m²) on the sample surface can be controlled by adjusting the distance between the xenon lamp and the round-shape reactor. The irradiation intensity was measured using a radiometer (FZ400, Beijing Changtuo Science and Technology Co., China). The high purity N₂ and O₂ with a total flow rate of 800 mL/min were introduced into the round-shape reactor. The relative humidity (RH, 7%–70%) was adjusted by altering the ratio of dry N₂ to wet N₂, and it was measured by a hygrometer (Center 314, Shanghai Shuangxu Electronics Co., LTD, China). The experimental temperature varied within the range of 278–308 K by circulating the temperature-controlled water at the bottom of the reactor and using the water bath outside of the reactor.

1.3. Gasses measurements

The NO₂ and NO were directly measured using a NO₂ chemiluminescence analyzer (THERMO 42i, Thermo Fisher Scientific, USA), which was equipped with a molybdenum converter. Because HONO will be detected as NO₂ by the NOₓ analyzer, a quartz tube (10 cm length, 0.6 cm inner diameter) filled with 1.0 g of crystalline Na₂CO₃ was connected between the round-shape reactor and the NOₓ analyzer. This Na₂CO₃ tube can
capture 99% of HONO at the steady state (Han et al., 2016). NO3, NO and HONO were detected by a bypass tube in one experiment, while NO and NO2 were measured by the Na2CO3 tube in another experiment. Thus, the HONO concentration can be obtained from the difference of the NO2 signals in two separate experiments with the same NO3 chemiluminescence analyzer. This method has been widely employed to measure the HONO concentration in previous studies (Bao et al., 2018; Brigante et al., 2008; Cazoir et al., 2014; Monge et al., 2016b; Yang et al., 2018; Zhou et al., 2018). A new Na2CO3 tube was installed to avoid saturation effects before each experiment. About 5% of NO2 in the experiments was captured by the Na2CO3 tube, which was considered in the calculations of NO2 and HONO emission flux density. HNO3 could also be converted to NO2 on the molybdenum surface and detected by the NO3 chemiluminescence analyzer (Steinbacher et al., 2007). In order to exclude HNO3 being captured by the Na2CO3 tube, a quartz tube filled with NaCl was also introduced to capture gaseous HNO3 (Yang et al., 2018). There were no differences for experimental results with or without the NaCl tube, suggesting that the formation of gaseous HNO3 was negligible.

1.4. NO2 and HONO emission flux density

The emission flux density (molecules/(cm2·sec)) of NO2 (RNO2) or HONO (RHONO) was defined as the number of NO2 or HONO molecules generated by the nitrates photolysis per unit area and time. Eqs. (1) and (2) were used to quantify the production of NO2 and HONO during the photolysis of nitrates, respectively,

\[ R_{\text{NO2}} = \frac{V_0 \times \int_{t_1}^{t_2} (C_{\text{NO2}} - C_{0,\text{NO2}}) \, dt \times N_A}{V_m \times S \times (t_2 - t_1)} \]  

\[ R_{\text{HONO}} = \frac{V_0 \times \int_{t_1}^{t_2} (C_{\text{HONO}} - C_{0,\text{HONO}}) \, dt \times N_A}{V_m \times S \times (t_2 - t_1)} \]  

where \( C_{\text{NO2}} \) and \( C_{\text{HONO}} \) (ppbV) are the NO2 concentration under irradiation and the steady-state NO2 concentration in the dark, respectively; \( C_{0,\text{NO2}} \) and \( C_{0,\text{HONO}} \) (ppbV) are the HONO concentration under irradiation and the steady-state HONO concentration in the dark, respectively; \( t_1 \) and \( t_2 \) (min) are the time when the light exposure experiment starts and ends, respectively; \( S \) (cm2) is the geometric area of the stainless steel sample dish; \( V_0 \) (mL/min) is the volume flow of gas; \( V_m \) (L/mol) is the molar volume of gas, depending on the temperature; \( N_A \) (6.022 × 1023 mol−1) is the Avogadro constant. Similar equations were also employed to obtain emission flux densities of NO2 and HONO in the photochemical processes (Yang et al., 2020; Ye et al., 2016a). Although there were slight differences in dimensional units for emission flux densities, they were essentially the same.

1.5. Analytical methods

The light absorption abilities of TiO2 with different crystal structures were recorded via the UV–visible diffuse reflectance spectrophotometer (UV–VIS DRS, UV-2550, Shimadzu, Japan) with BaSO4 as the standard reference. Mineral components of KNO3/TiO2/SiO2 were analyzed using the X-ray diffractometer (XRD, D/max-2500/PC, Rigaku, Japan) with Cu Kα radiation at 40 kV and 300 mA. Appendix A Fig. S3 displays the X-ray diffraction patterns, confirming that the sample was mainly composed of KNO3, TiO2 and SiO2.

2. Results and discussion

2.1. Influences of TiO2 crystal structures on NO2 and HONO emissions

Appendix A Fig. S4 shows the temporal changes of NO2, HONO and NO signals on KNO3/TiO2/SiO2, when rutile and anatase were used as TiO2, respectively. Upon exposure to light, the NO2 signal for rutile was only 0.6 ppbV (Appendix A Fig. S4a). By contrast, the NO2 signal for anatase had an obvious increase at the initial stage, and then it remained unchanged at about 41 ppbV in the irradiation time of 30–60 min. This suggests that rutile and anatase play different roles in the NO2 emission during the KNO3 photolysis. As shown in Appendix A Fig. S4b, there were slight HONO emissions on KNO3/TiO2/SiO2 under irradiation. The average HONO signal within 60 min was 0.8 and 1.0 ppbV for rutile and anatase, respectively. The NO signal was always negligible in the dark and under irradiation (Appendix A Fig. S4c).

Fig. 1 shows the RNO2 and RHONO on KNO3/TiO2/SiO2 as a function of the rutile or anatase mass ratio. The error bars in all figures represent the standard deviations of three independent experiments. As shown in Fig. 1a, RNO2 and RHONO markedly decreased from (2.99 ± 0.24) × 1011 to (1.13 ± 0.28) × 1011 to (5.72 ± 0.34) × 109 and (1.13 ± 0.11) × 1010 molecules/(cm2·sec) with increasing the rutile mass ratio from 0 to 8 wt.%, respectively. It is concluded that rutile significantly inhibits the NO2 and HONO emissions from the KNO3 photolysis.

Compared to the rutile, the anatase presented different influences on the NO2 and HONO emissions from the KNO3 photolysis. Fig. 1b shows that RNO2 and RHONO decreased to 0 and (1.46 ± 0.03) × 1010 molecules/(cm2·sec), respectively, when the anatase mass ratio increased to 0.5 wt.%. Nevertheless, with further increasing the anatase mass ratio to 8 wt.%, RNO2 sharply increased to (3.31 ± 0.13) × 1011 molecules/(cm2·sec), accompanied by a slight RHONO increase. These results indicate that the role of anatase in the NO2 and HONO emissions from the KNO3 photolysis greatly depends on the anatase mass ratio.

The dependence of NO2 and HONO emissions on the mixed crystals of TiO2 has been investigated as shown in Appendix A Fig. S5, where TiO2 consisted of rutile and anatase and its mass content was 5 wt.%. in KNO3/TiO2/SiO2. With decreasing the mass ratio of rutile to anatase from 4.0 to 0.25, RNO2 continuously increased from (0.79 ± 0.43) × 1010 to (1.18 ± 0.17) × 1011 molecules/(cm2·sec). By contrast, RHONO almost remain unchanged within experimental uncertainties and its average value was (1.23 ± 0.58) × 1011 molecules/(cm2·sec). It means that the mixed-states of rutile and anatase have important effects on the nitrates photolysis.

The photolysis pathways of nitrates were proposed according to experimental results and previous studies.
Fig. 1 – Emission flux density of NO$_2$ ($R_{\text{NO}_2}$) and HONO ($R_{\text{HONO}}$) on KNO$_3$/TiO$_2$/SiO$_2$ at different mass ratios of (a) rutile and (b) anatase. Reaction conditions: 10 wt.% KNO$_3$, irradiation intensity of 290 W/m$^2$, temperature of 298 K, and relative humidity (RH) of 40%.

Nitrites can accept photons and generate NO$_2$ and NO$_2^-$ (Reactions (3) and (4)). HONO was produced by the protonation process of NO$_2^-$ (Reaction (5)).

$\text{NO}_2^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-$  

(3)

$\text{NO}_2^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-$  

(4)

$\text{NO}_2^- + \text{H}^+ \rightarrow \text{HONO}$  

(5)

The photolysis of nitrates in the presence of TiO$_2$ can be explained by Reactions (6)-(9). TiO$_2$ accepted photons to form electron ($e^-_{\text{cb}}$) and hole ($h^+_{\text{vb}}$) pairs under irradiation (Reaction (6)) [Bedjanian and El Zein, 2012; Moon et al., 2019; Ndour et al., 2009a], which would change chemical reaction channels of the nitrates photolysis (Ndour et al., 2009a). The holes ($h^+_{\text{vb}}$) interacted with H$_2$O to produce HO• and H$^+$ (Reaction (7)) [El Zein and Bedjanian, 2012a]. NO$_2$ reacted with the holes ($h^+_{\text{vb}}$) to generate NO$_3^-$ radicals (NO$_3^+$) (Reaction (8)) [Ndour et al., 2009a], which would be decomposed to yield NO$_2$ and oxygen radicals (O•) under irradiation (Reaction (9)). NO$_2$ accepted the electrons ($e^-_{\text{cb}}$) to form NO$_2^-$ (Reaction (10)) [Bedjanian and El Zein, 2012], and then NO$_2$ and HONO would be produced by the reactions of NO$_2^-$ with HO• (Reaction (11)) and H$^+$ (Reaction (5)) [Bedjanian and El Zein, 2012], respectively.

$\text{TiO}_2 + h\nu \rightarrow e^-_{\text{cb}} + h^+_{\text{vb}} + \text{TiO}_2$  

(6)

$\text{H}_2\text{O} + h^+_{\text{vb}} \rightarrow \text{HO}^• + \text{H}^+$  

(7)

$\text{NO}_2^- + h^+_{\text{vb}} \rightarrow \text{NO}_3^- + \text{H}^+$  

(8)

$\text{NO}_3^- + \text{H}^+ \rightarrow \text{NO}_2^- + \text{O}^-$  

(9)

$\text{NO}_2^- + e^-_{\text{cb}} \rightarrow \text{NO}_2$  

(10)

$\text{NO}_2^- + \text{HO}^• \rightarrow \text{NO}_2 + \text{OH}^-$  

(11)

According to the reaction mechanism above, $R_{\text{NO}_2}$ and $R_{\text{HONO}}$ by the nitrates photolysis should be enhanced in the presence of TiO$_2$. However, compared with that on KNO$_3$/SiO$_2$, $R_{\text{NO}_2}$ and $R_{\text{HONO}}$ on KNO$_3$/TiO$_2$/SiO$_2$ exhibited a significant decrease, when the rutile and anatase mass ratio was less than 8 and 0.5 wt.%, respectively (Fig. 1). This may be ascribed to secondary heterogeneous uptake of NO$_2$ and HONO generated in situ from the nitrates photolysis on the TiO$_2$ surface. To identify this assumption, the photochemical uptake of NO$_2$ on rutile and anatase was examined as shown in Appendix A Fig. S6. It was clearly observed that the NO$_2$ concentration drastically decreased upon exposure to TiO$_2$ under irradiation, confirming that light obviously enhanced the uptake of NO$_2$ on TiO$_2$. Previous studies also demonstrated photo-enhanced reaction of NO$_2$ on TiO$_2$ and grime (El Zein and Bedjanian, 2012a; Liu et al., 2019a, 2020; Ndour et al., 2008, 2009b). The photochemical conversions of NO$_2$ to HONO and HNO$_3$ on TiO$_2$ can be described using the Reactions (6), (7), (12) and (13) [Bedjanian and El Zein, 2012; Devahasdin et al., 2003; Ndour et al., 2008; Ohko et al., 2008].

$\text{NO}_2 + e^-_{\text{cb}} + \text{H}^+ \rightarrow \text{HONO}$  

(12)

$\text{NO}_2 + \text{HO}^• \rightarrow \text{HNO}_3$  

(13)

The KNO$_3$ photolysis (Fig. 1) and the secondary photochemical uptake of NO$_2$ on TiO$_2$ (Appendix A Fig. S6) contributed to the HONO formation. The conversion of NO$_2$ to HONO on the illuminated TiO$_2$ surface has been reported (Bedjanian and El Zein, 2012; Gustafsson et al., 2006; Monge et al., 2010a). However, the secondary uptake of HONO generated in situ can occur on the TiO$_2$ surface under irradiation (El Zein et al., 2013; El Zein and Bedjanian, 2012b), which led to the decrease in $R_{\text{HONO}}$ during the KNO$_3$ photolysis in the presence of TiO$_2$. As shown in Fig. 1b, $R_{\text{NO}_2}$ and $R_{\text{HONO}}$ had an increase with the anatase mass ratio ranging from 1 to 8 wt.%, which was in contrast to the effect of rutile on $R_{\text{NO}_2}$ and $R_{\text{HONO}}$. This means that anatase plays a more significant enhancement role in the KNO$_3$ photolysis than the secondary photochemical uptake of NO$_2$ and HONO at a larger anatase mass ratio. Nitrates mixed with TiO$_2$ are a complex reaction system,
where photolysis and photochemical uptake occur simultaneously. Both the formation of gaseous NO\textsubscript{2} and HONO by the nitrates photolysis (Fig. 1) and the photochemical uptake of NO\textsubscript{2} on rutile or anatase (Appendix A Fig. S6) demonstrated that NO\textsubscript{2} and HONO were not completely recycled back to nitrates through the photocatalytic reaction on TiO\textsubscript{2}. Therefore, nitrates were consumed during the photolysis process in the presence of TiO\textsubscript{2}.

To understand the reasons for different effects of rutile and anatase on the nitrates photolysis, the light absorption property of TiO\textsubscript{2} was measured as shown in Appendix A Fig. S7. According to the UV–VIS DRS, the band gap of TiO\textsubscript{2} was calculated and summarized in Appendix A Table S1. The rutile, anatase, and their mixtures had similar band gap between 3.21 and 3.36 eV. The band gap of semiconductor photocatalysts determined their ability of light absorption (Ahmadi et al., 2019; Maisano et al., 2016) and the generation of electron and hole pairs (Tayade et al., 2007). This indicates that the slight difference in the light absorption property of rutile and anatase have a minor effect on their photocatalytic activity for the nitrates photolysis. The discrepancy of rutile and anatase in the influences on the nitrates photolysis may originate from their special physicochemical properties, such as surface and electronic structure (Etacheri et al., 2015; Tayade et al., 2007), stability (Etacheri et al., 2015), reduction and oxidation ability (Diebold, 2003; Henderson, 2011), and recombination rate of photo-generated electron-hole pairs (Karthikeyan et al., 2017; Katal et al., 2020). It has been proved that anatase generally had higher photocatalytic activity than rutile (Tayade et al., 2007).

2.2. Influences of environmental factors on NO\textsubscript{2} and HONO emissions

In order to further characterize the nitrates photolysis, the NO\textsubscript{2} and HONO emissions on KNO\textsubscript{3}/SiO\textsubscript{2} mixed with rutile and anatase were measured under different environmental conditions. Fig. 2 shows R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} as a function of the KNO\textsubscript{3} mass ratio. With increasing the KNO\textsubscript{3} mass ratio from 1 to 20 wt.%, R\textsubscript{NO\textsubscript{2}} increased from (8.54 ± 1.00) × 10\textsuperscript{10} to (1.82 ± 0.21) × 10\textsuperscript{11} molecules/(cm\textsuperscript{2}·sec). R\textsubscript{HONO} had a slight increase with the KNO\textsubscript{3} mass ratio ranging from 1 to 5 wt.%, while it almost remained unchanged at (1.96 ± 0.34) × 10\textsuperscript{10} molecules/(cm\textsuperscript{2}·sec) in the KNO\textsubscript{3} mass range of 5–20 wt.%.

Fig. 3 displays R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} on KNO\textsubscript{3}/TiO\textsubscript{2}/SiO\textsubscript{2} at different irradiation intensity. R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} exhibited an increase trend with irradiation intensity. R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} increased from (5.32 ± 0.30) × 10\textsuperscript{10} and (1.06 ± 0.56) × 10\textsuperscript{10} molecules/(cm\textsuperscript{2}·sec) at 80 W/m\textsuperscript{2} to (1.49 ± 0.28) × 10\textsuperscript{11} and (4.61 ± 0.81) × 10\textsuperscript{10} molecules/(cm\textsuperscript{2}·sec) at 400 W/m\textsuperscript{2}, respectively. The increase of irradiation intensity provided more photons for the KNO\textsubscript{3} photolysis and the generation of electron and hole pairs on TiO\textsubscript{2}, which led to more NO\textsubscript{2} and HONO emissions by reactions (3)–(11).

As shown in Fig. 4, both R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} increased with RH ranging from 7% to 55%, and decreased from 55% to 70% RH. The maximum values of R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} at RH = 55% were (1.69 ± 0.08) × 10\textsuperscript{11} and (2.98 ± 1.65) × 10\textsuperscript{10} molecules/(cm\textsuperscript{2}·sec), respectively. The increase in RH would enhance the formation of •OH and H\textsuperscript{+} by the reaction of H\textsubscript{2}O with h\textsubscript{vb} (Reaction (7)) (Ndour et al., 2009a). Thus, more NO\textsubscript{2} and HONO was produced by the reaction of NO\textsubscript{2} with •OH (Reaction (11)) and the protonation process of NO\textsubscript{2} with H\textsuperscript{+} (Reaction (5)), respectively. This contributes to the increase in R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} with RH in the range of 7%–55%. It has been reported that the photolysis of nitrates under humid conditions was faster than that under dry conditions (Rubasinghege and Grassian, 2009). The scavenging of the holes (h\textsubscript{vb}) by H\textsubscript{2}O (Reaction (7)) was enhanced when the RH continuously increased to 70% (Ndour et al., 2009a). This would inhibit the reaction of NO\textsubscript{2} and h\textsubscript{vb} to produce NO\textsubscript{3} (Reaction (8)), hindering the formation of NO\textsubscript{2} and HONO in Reactions (9–11). In addition, the disproportionation reaction between NO\textsubscript{2} and H\textsubscript{2}O adsorbed on the surface became more significant. More NO\textsubscript{2} and HONO would be dissolved in the adsorbed H\textsubscript{2}O. Accordingly, R\textsubscript{NO\textsubscript{2}} and R\textsubscript{HONO} decreased with increasing the RH to 70%.
3. Conclusions and atmospheric implications

The rutile and anatase had different effects on $R_{\text{NO}_2}$ and $R_{\text{HONO}}$, suggesting significant dependence of the KNO3 photolysis on TiO2 crystal structures. The NO2 and HONO emissions from the KNO3 photolysis relied on various environmental conditions, including KNO3 mass, irradiation intensity, temperature and RH. These findings would be helpful to understand the atmospheric lifetime of nitrates and the role of nitrates in the reservoirs of NO2 and HONO in the real environment.

The atmospheric lifetime ($\tau$) of nitrates can be calculated by the following equations (Ye et al., 2017),

\[ N_{\text{nitrates}} = N_{\text{nitrates, total}} \times \frac{h}{H} \]  

\[ H = \frac{m}{\rho \times S} \]  

\[ J_{\text{nitrates}} = \frac{(R_{\text{NO}_2} \times M_{\text{NO}_2} + R_{\text{HONO}} \times M_{\text{HONO}}) \times S}{N_A \times N_{\text{nitrates}}} \]  

\[ \tau = \frac{1}{J_{\text{nitrates}}} \]  

where $N_{\text{nitrates}}$ (g) is the mass of nitrates photolyzed in the reaction; $N_{\text{nitrates, total}}$ (g) is the total mass of nitrates used in the experiments; $h$ (nm) is the nitrates coating thickness where light can reach, and it was assumed to be 100 nm; $H$ is the total thickness of the sample coating containing TiO2 (231.40 μm) or without TiO2 (237.40 μm); $m$ (g) is the total mass of sample; $\rho$ is the mixture density of KNO3/TiO2/SiO2 (2.247 g/cm3) or KNO3/TiO2 (2.19 g/cm3), which is calculated according to the density and the mass ratio of each substance; $S$ (cm2) is the geometric area of the stainless steel sample dish; $J_{\text{nitrates}}$ (sec−1) is the photolysis rate constant; $M_{\text{NO}_2}$ (g/mol) and $M_{\text{HONO}}$ (g/mol) are the molar mass of NO2 and HONO, respectively. Under environmental conditions with irradiation intensity of 290 W/m2, 298 K, 40% RH, KNO3 mass of 10 wt.% and TiO2 mass of 5 wt.% (the mass ratio of rutile to anatase was 1:4), the photolysis rate constant and atmospheric lifetime of nitrates were calculated to be $3.6 \times 10^{-6} – 5.8 \times 10^{-6}$ sec−1 and 47.9–77.2 hr, respectively. They were estimated to be $1.3 \times 10^{-5}$–$1.6 \times 10^{-5}$ sec−1 and 17.4–21.4 hr in the absence of TiO3, respectively. This photolysis rate constant was larger than that with TiO3, which was ascribed to lower NO2 and HONO emissions due to their secondary photochemical uptake on TiO2. The photolysis rate constants obtained here were within the range $(6.0 \times 10^{-6} – 5.0 \times 10^{-4}$ sec−1) of that of nitrates and nitric acids in low-NOx environments (Ye et al., 2016a, 2017; Zhou et al., 2003). The calculated atmospheric lifetime of nitrates without TiO3 was close to that (15 hr) of total nitrates in real atmospheric aerosols (Ye et al., 2017).

Assuming the aerosol surface concentration of $10^2$–$10^3$ μm2/cm3 (Stemmler et al., 2007) and the nitrates content of 10 wt.% in the continental aerosols (Poullain et al., 2011; Revuelta et al., 2012; van Pinxteren et al., 2009; Wang et al., 2015), the source strength of NO2 and HONO from the photolysis of nitrates in aerosols without TiO2 was estimated.
to be 3.7–43.2 and 1.1–18.9 pptV/hr under the environmental conditions above, respectively. For the nitrates photolysis in aerosols containing TiO$_2$, it was calculated to be 1.4–18.1 and 0.1–4.6 pptV/hr for NO$_2$ and HONO, respectively. The NO$_2$ formation (30 pptV/hr) from the photolysis of HNO$_3$ deposited on the ground and vegetation surfaces was within the source strength of NO$_2$ from the photolysis of nitrates with or without TiO$_2$ (Zhou et al., 2003). The HONO source strength was 70–200 pptV/hr (Sörgel et al., 2015; Zhang et al., 2012; Zhou et al., 2011) and 1–10 ppbV/hr (Elehorgany et al., 2010; Villena et al., 2011) in rural areas and urban areas, respectively, which was much greater than the HONO formation from the photolysis of nitrates with or without TiO$_2$. This work clearly confirmed that TiO$_2$ played important roles in NO$_2$ and HONO emissions from the nitrates photolysis. Other minerals with photocatalytic activity, such as Fe$_2$O$_3$ and ZnO, should be also further investigated to determine their influences on the nitrates photolysis.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.09.016.

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