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Comprehensive Study about the Photolysis of Nitrates on Mineral Oxides

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nitrates like $Fe(NO_3)_3$, $Ca(NO_3)_2$, and KNO_3 . SO_2 and water vapor promote the photodegradation by increasing the surface acidity due to the photoinduced formation of H_2SO_4 /sulfate and H^+ , respectively. O_2 enables the photo-oxidation of NO_x to regenerate nitrate and thus inhibits the NO_x yield. Overall, our results demonstrated that the photolysis of nitrate can be accelerated under complex air pollution conditions, which are helpful for understanding the transformation of nitrate and the nitrogen cycle in the atmosphere.

KEYWORDS: photolysis, nitrate, renoxification, cation effect, SO₂, TiO₂

INTRODUCTION

Nitrogen oxides ($NO_x = NO_2 + NO$) mainly come from vehicle exhaust and industrial emissions and play a key role in the atmospheric chemistry.¹ NO_x are the main precursors of atmospheric photochemical smog^{2,3} and have an important contribution to the formation of haze^{4,5} and acid rain,^{6,7} which make them the crucial factors affecting regional air quality. Therefore, it is of great environmental significance to study the transformation of nitrogen oxides in the atmosphere, especially their source and sink processes. The transformation of nitrogen oxides into nitrates is the most important sink of NO_{x}^{8} which has a direct impact on the atmospheric lifetime and environmental impact of nitrogen oxides. There are several well-known conversion pathways of nitrogen oxides into nitrates. One is the oxidation of NO₂ by OH radicals, resulting in the formation of $HNO_{3}^{9,10}$ which can adsorb or deposit on the surface of particles^{11,12} or form ammonium nitrate by combining with ammonia.^{13,14} Another pathway is the oxidation of NO_x by O_3 to form N2O5, which is then hydrolyzed on the surface of particles to form nitrate.^{15–17} The third process is the heterogeneous transformation of nitrogen oxides on the surface of particles to form nitrates.^{18,19}

On the other hand, the conversion of nitrates to NO_x, namely, renoxification, has attracted much attention. For example,

Finlayson-Pitts and co-workers have studied the reaction of NO with HNO₃ on a porous glass and found the formation of gaseous NO₂ and HONO in this reaction.^{20–22} In addition, several recent studies also found that the humidification and dehumidification process of mixed particles including nitrate and organic acids can convert particulate nitrate to gaseous HNO₃.^{23–26} More importantly, many recent studies highlighted the photochemical renoxification in the atmosphere mainly due to its potential contribution to the daytime HONO^{27–31} and heterogeneous sulfate formation.^{32,33} In fact, the photochemical conversion of nitrate into NO_x or HONO has been found in many atmospheric environmental media, such as atmospheric particulate matters,^{30,34–37} ice and snow,^{38–40} building surfaces,²⁸ plant leaves,^{41,42} urban grime,²⁷ and solutions.

It was found that the photolysis rate of HNO_3 adsorbed on atmospheric particles is 1–3 orders of magnitude higher than that of gaseous HNO_3 or nitrate ion in solution.^{27,29,43,46,47}

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These results also imply that the discrepancy of photolysis rate of nitrate under different reaction conditions is about 3 orders of magnitude, indicating significant differences in the photolysis mechanism. There are several reasons for the differences in the photolysis rate of nitrate. First, the chemical composition of substrates is complex and diverse, which significantly determined the photolysis of nitrate. Second, there are various kinds of nitrate in the atmospheric particles depending on the combined cation. In addition, environmental factors like temperature, relative humidity (RH), and coexisting species may also affect the photolysis of nitrate. Therefore, further research on the photolysis mechanism of nitrate on different types of particles is urgently needed.

Mineral dust, originated from arid and semiarid regions, represents one of the largest mass fractions of the global aerosols.^{48,49} Substantial evidence shows that mineral dust has an important influence on the atmospheric chemical processes of NO_x .^{19,50} Model simulation results suggested that the interaction with mineral dust can greatly affect the concentration of NO_3 , N_2O_5 , and HNO_3 .^{17,51–53} Field observations always detected the association of nitrate with mineral dust.^{54–57} The heterogeneous reactions of NO_2 , N_2O_5 , and HNO_3 on mineral dust have also been verified in laboratory experiments.^{17,58–60} It should be noted that the chemical composition of mineral dust particles is close to that of soil,^{48,49} which is an important sink of atmospheric nitrogen deposition.⁶¹ Thus, the chemistry of nitrate on mineral dust could also represent the conditions on soil.

Several previous studies have focused on the mechanism of the photolysis of nitrate associated with mineral oxides as well as the effect of reaction conditions like RH and light wavelength. $^{36,62-67}$ It should be noted that the nitrate studied in these studies was adsorbed nitric acid. Considering the transformation of adsorbed nitric acid to nitrate salts in the transport of atmospheric particulate matters, the effect of cations other than hydrogen ions should be further explored. In this study, typical mineral oxides $(SiO_2, Al_2O_3, and TiO_2)$ were chosen as representative of mineral dust to study the photolysis of nitrate associated with mineral dust or deposited on the ground surface. The photolysis processes of nitrates with different cations were compared to elucidate the effect of cations on the photolysis of nitrates. In addition, the influence of typical environmental conditions was also investigated. This study provides useful information for understanding the photolysis of nitrate in the atmosphere.

MATERIALS AND METHODS

Samples. The chemical agents, all with analytical grade, NH_4NO_3 , $Fe(NO_3)_3$, $Ca(NO_3)_2$, KNO_3 , $a-Al_2O_3$, and SiO_2 from Sinopharm Chemical Reagent Co., Ltd. and TiO₂ (P25: 80% anatase, 20% rutile, Degussa) were used as purchased. The nitrate and oxides were mixed by dispersing a total mass of 1.0 g of oxide powder and 0.02 g of nitrate in 50.0 mL of ultrapure water. The mixed slurry was dripped onto a quartz tube inner wall (20.0 cm length, 1.1 cm i.d.) and dried in an oven at 373 K for 1 h. The ion chromatography measurement results showed that the amount of nitrate in these mixed particles was about 1.9-2.0 wt %. The images and Raman spectra of NH₄NO₃ and its mixture with TiO₂ prepared were analyzed by micro-Raman spectrometry (Renishaw InVia Raman microscope) and the results are shown in Figures S1 and S2 in the supplementary information, respectively. These Raman characterization results indicated that the form of nitrate was kept during the sample

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preparation process. These dried particles were used for flow tube and in situ diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) experiments. SO₂ (10 ppmv + N₂, Beijing Huayuan), NO₂ (50 ppmv + N₂, Beijing Huayuan), NO (50 ppmv + N₂, Beijing Huayuan), NH₃ (50 ppmv + N₂, Beijing Huayuan), O₂ (99.999%, Beijing Huayuan), and N₂ (99.999%, Beijing Huayuan) were used as received. The RH was controlled by regulating the ratio of dry and wet stream flow, which was recorded during the whole experiment by a hygrometer (HMP110, Vaisala).

Flow Tube Reactor. The photolysis reaction of nitrates was performed in a horizontal cylindrical coated-wall flow tube reactor, which has been described in detail elsewhere.^{68,69} Briefly, the tube with the deposited 2 wt % nitrate/oxide mixture sample was placed into the main reactor along its axis. Synthetic air or N₂ was used as the carrier gas, which was introduced into the flow tube reactor at a total flow rate of 1800 mL·min⁻¹. The flow tube was surrounded by six UV lamps (365 nm, T5, UVA, 8 W) with a broad UV emission spectrum between 330 and 420 nm. The irradiance intensity in the reactor was $1.27 \text{ W} \cdot \text{m}^{-2}$ at 370 nm. A NO, analyzer (THERMO 42i) was used to monitor the products of NO_x online during the photolysis. For HONO, an in-house HONO analyzer was employed, which has been used in several field measurements previously.^{70,71} NH₃ was monitored by a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS, Aerodyne Research).7

The observed production rates $(10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{mg}^{-1})$ of HONO (P_{HONO}) and NO_x (P_{NO_x}) were calculated by eqs I and II, respectively^{29,30}

$$P_{\text{HONO}} = \frac{F_{\text{g}}}{60 \times 1000 \times (t_2 - t_1) \times R \times T} \times \int_{t_1}^{t_2} C_{\text{HONO}} dt$$
(I)

$$P_{\text{NO}_{x}} = \frac{F_{\text{g}}}{60 \times 1000 \times (t_{2} - t_{1}) \times R \times T} \times \int_{t_{1}}^{t_{2}} C_{\text{NO}_{x}} dt$$
(II)

where $F_{\rm g}$ is the carrier air flow rate (L·min⁻¹) through the reactor, R is the gas constant, and T is the absolute temperature (K); t_1 and t_2 (min) are the starting and ending times of the irradiation, respectively. The total reaction time for each experiment was set to 60 min. $C_{\rm HONO}$ and $C_{\rm NO_x}$ (ppbv·mg⁻¹) are the online measured concentrations of HONO and NO_x normalized to the sample mass. The uncertainties of $P_{\rm HONO}$ and $P_{\rm NO2}$ are calculated according to the measurement errors of flow rate, temperature, and product concentrations in eqs I and II, respectively.

In Situ DRIFTS. The photolysis reaction of mixed NH_4NO_3 and TiO_2 particles was also investigated by in situ diffuse reflectance Fourier-transform infrared spectroscopy (in situ DRIFTS, is50, Thermo Fisher Scientific), equipped with an in situ diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N_2 . Before the experiment, the particles were finely ground and placed into a ceramic crucible in the in situ chamber. The samples were first pretreated at 373 K for 120 min in a stream of synthetic air or N_2 gases in a total flow of 200 mL·min⁻¹ to remove weakly adsorbed species. After the sample was cooled to room temperature (295 K), the UV light was turned on to start the photolysis reaction.

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Figure 1. Production of NO₂, NO, and HONO during the photolysis of NH₄NO₃ on (A) TiO₂, (B) Al₂O₃, and (C) SiO₂ particles at 15% RH.



Figure 2. Observed production rates of (A) NO2 and (B) HONO in the photolysis of various nitrates on TiO2 at various RHs in air.

Infrared spectra were collected using a computer with OMNIC 6.0 software (Nicolet Corporation). All spectra were recorded at a resolution of 4 cm⁻¹ for 100 scans in the spectral range of 600–4000 cm⁻¹, and then Kubelka–Munk (K–M) conversion was conducted.

RESULTS AND DISCUSSION

Photolysis of NH₄NO₃ on Mineral Oxides. First, the photolysis of NH₄NO₃ on the surface of TiO₂, Al₂O₃, and SiO₂ samples at room temperature (295 K) and RH = 15% was studied using the flow tube reactor. The formation of NO_{2} HONO, NO, and NH₃ as a function of photolysis time is shown in Figure 1. The concentration of these gaseous products was normalized to the sample mass. It is found that the concentrations of gaseous products produced by the photolysis of NH₄NO₃ on SiO₂ and Al₂O₃ are much less than those on TiO₂. This suggests that the photocatalytic activity of TiO₂ plays an important role in the photodegradation of nitrate. In the case of NH₄NO₃/TiO₂ mixture, when the UV lamps were turned on, the concentrations of NO₂, NO, and HONO increased rapidly and then gradually decreased with increasing illumination time. The concentration of NO₂ was the highest, followed by HONO and NO. Thus, NO2 is the primary photolysis product of NH₄NO₃ on TiO₂. It is interesting to note that there were two concentration peaks of NO₂, which were synchronous with the sole concentration peaks of HONO and NO, respectively. These results indicate that there are two different formation pathways of NO₂ in the photolysis of NH₄NO₃ on TiO₂. One is the decomposition of NO_3^- and the other is the photo-oxidation of NH4⁺, as discussed later. Meanwhile, no increase in the

concentration of $\rm NH_3$ suggests that there is a heterogeneous photochemical conversion process of ammonium with a product other than ammonia. The relationship between the conversion of ammonium and the photolysis of nitrate will be discussed later.

Compared to TiO₂, the formation of NO and NO₂ is not obvious in the photolysis of NH₄NO₃ on SiO₂ and Al₂O₃. Meanwhile, a little HONO was observed as a product in the photolysis of NH₄NO₃ on SiO₂, suggesting the ubiquitous formation of HONO in the photolysis of nitrate, even on a substrate without high photocatalytic activity, and regardless of whether there is an obvious formation of NO_x or not. In a previous study, Bao et al.³⁰ found that HONO was the main product, while NO₂ was almost undetectable during the photochemical aging process of the Beijing urban PM_{2.5} aerosol particles. They proposed a reduction mechanism that water and hydrogen ion promoted photoreduction of HNO₃ to HONO. In addition, they further evaluated the effect of different heterogeneous surfaces on HONO and NO₂ production during photolysis of HNO₃ loaded on different substrate surfaces. It was found that no HONO or NO2 was released in the HNO3 loaded on quartz microfiber filters and pyrex glass, while significant NO₂ production and negligible HONO were detected on the surface of TiO₂ and Al₂O₃ under irradiation. The difference between our results and Bao's indicates that cations have an important influence on the photolysis products of nitrate.

Effects of Cations and RH on the Photolysis of Nitrates on TiO₂. In addition to NH₄NO₃, there are other types of nitrates in the atmosphere. When the concentration of ammonia in the air is insufficient or the concentration of sulfuric acid is



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Figure 3. Observed production rates of (A) NO_2 and (B) HONO during the photolysis of NH_4NO_3 on TiO_2 particles under various RHs with or without 100 ppb SO_2 .

high, the conversion of gaseous HNO₃ to NH₄NO₃ will be inhibited.⁷³ At this time, the condensation of HNO₃ on mineral particles could result in the formation of various nitrate species, such as $Ca(NO_3)_2$, KNO_3 , and $Fe(NO_3)_3$ on mineral dust.^{19,74} In the present study, the photolysis of $Ca(NO_3)_{21}$ KNO₃, and $Fe(NO_3)_3$ on TiO₂ was also studied using a flow tube reactor. The changes in the concentration of NO_x and HONO are shown in Figure S3. It was found that NO₂ was the main product, similar to those of NH₄NO₃. However, there was only one concentration peak of NO₂. Meanwhile, NO was not produced in the photolysis of all of these three nitrate species. The yield of NO_2 and HONO was largest from $Fe(NO_3)_3$ and then $Ca(NO_3)_2$ and KNO_3 , suggesting that the cations could significantly affect the photolysis of nitrate. In a previous study, Richards-Henderson et al.⁷⁵ found that cations impact the NO₂ production from the photolysis of aqueous thin water films of nitrate salts because of the possible impacts on the concentration of nitrate ions in the interface region. Therefore, we further studied the effect of cations and RH on the photolysis of nitrates on TiO₂.

Figure 2 compares the observed production rates of NO₂ and HONO in the photolysis of KNO₃, $Ca(NO_3)_2$, $Fe(NO_3)_3$, and NH_4NO_3 under different RH. The P_{NO_3} and P_{HONO} of $Fe(NO_3)_3$ increased from 1.69×10^{-7} and 3.37×10^{-9} to 5.56×10^{-7} and 9.87×10^{-8} with the increase of RH from <5 to 65%, respectively. The $P_{\rm NO_2}$ and $P_{\rm HONO}$ of NH₄NO₃ increased from 3.04×10^{-7} and 3.42×10^{-9} to 1.44×10^{-6} and 9.52×10^{-8} with the RH changing from <5 to 35%, which then decreased to 5.60 $\times 10^{-7}$ and 8.30×10^{-9} at 80% RH, respectively. The P_{NO}, and $P_{\rm HONO}$ of Ca(NO₃)₂ increased from 3.30×10^{-7} and 2.37×10^{-9} to 4.71×10^{-7} and 2.68×10^{-8} with the RH changing from <5 to 25% which then decreased to 2.25×10^{-7} and 1.41×10^{-8} at 65% RH, respectively. The inhibition effect of water on the photolysis at high RH could be due to the deliquescence of nitrate on the surface. The deliquescence points for NH₄NO₃ and $Ca(NO_3)_2$ are $62\%^{76}$ and 18% RH,⁷⁷ respectively. When the RH is higher than the deliquescence point of nitrate, it will lead to the dissolution of nitrate, thus affecting the photolysis reaction. As for $Fe(NO_3)_3$, there is no data about its hygroscopic behavior. The growth factors of $Fe(NO_3)_3$ measured through a hygroscopic tandem differential mobility analyzer (HTDMA)²⁶ showed that it does not deliquesce in the RH range of 0-80% (Figure S4). Thus, the influence of RH on the photolysis of nitrate depends on the hygroscopicity of particles. The reason

may be that the dissolution effect makes the bonding interaction between nitrate and $\rm TiO_2$ weak and then reduces its reduction.

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Moreover, the observed production rates of NO2 and HONO of these nitrates were in the following order: $NH_4NO_3 >$ $Fe(NO_3)_3 > Ca(NO_3)_2 > KNO_3$. The measured pH of the saturated solution of these nitrates is in the following order: $KNO_3 > Ca(NO_3)_2 > NH_4NO_3 > Fe(NO_3)_3$. It implies the alkalinity of nitrate salts could significantly affect the production rates of NO₂ and HONO. The oxides or hydroxides of alkali metals (K^+, Ca^{2+}) left after the photodegradation of nitrate have strong alkalinity and can adsorb the formed HONO and NO₂. Although Fe³⁺ has been considered to have photochemical activity, the direct decomposition of $Fe(NO_3)_3$ without TiO_2 showed no obvious gaseous products like NO₂ and HONO. This suggests that the contribution of Fe^{3+} in this reaction may not be important. It should be noted that both the production rates of NO₂ and HONO from NH₄NO₃ are higher than those from $Fe(NO_3)_3$. This does not comply with the law of alkalinity and is due to the contribution of ammonium to the production of NO₂ and HONO.

It was proposed that the photolysis of nitrate ions in bulk aqueous solutions produces NO_2 and O^- via reaction 1, or NO_2^- and $O(^{3}P)$ through reaction 2^{78}

NO₃⁻ +
$$hv$$
 (λ > 280 nm) → NO₂ + O⁻ (1)
→NO₂⁻ + O(³P) (2) (1)

However, on the surface of TiO_2 , the high yields of HONO and NO₂ indicate that the existence of TiO_2 can greatly change the photolysis pathway of nitrate. It is well known that photoinduced electrons (e⁻) and holes (h⁺) can be generated on the surface of TiO_2 upon irradiation

$$\mathrm{TiO}_{2} + h\nu \to \mathrm{h}^{+} + \mathrm{e}^{-} \tag{3}$$

These photoinduced electrons and holes could promote the photolysis of nitrate on $\rm TiO_2$ as follows $^{65,79-81}$

$$NO_3^- + h^+ \to NO_3 \tag{4}$$

$$NO_3 + hv (<640 \text{ nm}) \rightarrow NO_2 + O \tag{5}$$

$$NO_3 + hv (585 - 640 \text{ nm}) \rightarrow NO + O_2$$
 (6)

$$NO_2 + e^- \to NO_2^- \tag{7}$$

The promotion effect of water on the photolysis within the RH range below the deliquescence point is mainly due to the

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Figure 4. (A) Observed production rates of NO_2 , NO, and HONO during the photolysis of NH_4NO_3 on TiO_2 particles at 15% RH in the presence and absence of O_2 . (B) DRIFTS spectra of TiO_2 exposed to 1 ppm NO_2 , NO, and NH_3 , respectively, for 4 h at 15% RH in the presence of UV irradiation and air.



Figure 5. (A) Concentration changes of NO_2 during the photolysis of NH_4NO_3 on TiO_2 particles at 15% RH in air and N_2 stream. (B) DRIFTS spectra of NH_4NO_3/TiO_2 upon UV irradiation for 1 h at 15% RH in air and N_2 stream.

enhancement of surface acidity by H^+ , which is produced by the photochemical reaction between the hole and water on TiO_2

$$H_2O + h^+ \to H^+ + OH \tag{8}$$

$$NO_2^- + H^+ \leftrightarrow HONO$$
 (9)

The formation of H⁺ on the surface can facilitate the transfer of the surface nitrite to HONO. As for NO₂, increase in the surface water can increase the observed production rate since increasing RH could reduce the uptake of NO₂ on TiO₂.⁸²

On the other hand, the effect of surface acidity on the photolysis was further verified by the effect of SO₂ on the photolysis of NH4NO3 on TiO2. SO2 is ubiquitous in the atmosphere and can be converted to sulfate on TiO₂ through the photochemical oxidation reaction.^{69,83,84} It is considered that the formation of sulfate always increases the acidity of the surface.⁸⁵ In this study, the photolysis of NH_4NO_3 on TiO_2 in the presence of 100 ppb SO₂ was investigated by a flow tube reactor. Figure 3 compares the observed production rates of NO2 and HONO in the photolysis reaction with and without SO₂. The production rates of NO₂ and HONO increased 1.2-1.5 and 2-10 times, respectively, due to the coexisting SO₂. In other words, SO₂ can promote the photolysis of NH₄NO₃ on TiO₂, especially the yield of HONO. The possible reasons are as follows. First, the sulfate generated by SO₂ oxidation (Figure S5 in the Supporting Information) could replace the surface nitrite and then promote the conversion of nitrite to HONO.³⁰ Second, the increasing surface acidity due to the formation of sulfate could shift the nitrite/HONO equilibrium. Third, the sulfate

formed can occupy the surface site⁶⁹ and inhibit the regeneration of nitrate.

Role of O₂ and the Regeneration of Nitrate on the Surface. To verify that nitrate may regenerate through the photochemical oxidation of NO_x in the photolysis process, the observed production rates of NO, NO₂, and HONO during the photolysis of NH₄NO₃ on TiO₂ in air and nitrogen at 15% RH are compared in Figure 4A. In the absence of O_{24} the observed production rates of NO, NO₂, and HONO increased by 20, 9, and 8 times, respectively. These results suggest that O2 has a reducing effect on the net consumption of nitrate because O₂ can promote the regeneration of nitrate through photooxidation of these gaseous products. This was further confirmed by the photochemical heterogenous reaction of NO and NO₂ on TiO_2 . As seen in Figure 4B, the exposure of TiO_2 to NO, NO₂, and NH₃ in air upon UV irradiation produces surface nitrate species with peaks at 1614, 1588, 1490, 1288, and 1248 cm^{-1.86,87} The formation of nitrate was due to the photooxidation reaction on TiO₂

$$2NO_2 + O_2 + 2e^- \rightarrow 2NO_3^- \tag{10}$$

$$NO + O_2 + e^- \to NO_3^- \tag{11}$$

$$2\mathrm{NH}_3 + 3\mathrm{O}_2 \to \mathrm{NO} + \mathrm{NO}_2 + 3\mathrm{H}_2\mathrm{O} \tag{12}$$

Therefore, when N_2 was used as the carrier gas, the reverse photochemical oxidation of NO and NO_2 to nitrate on the surface would be restricted.

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Oxidation of Ammonium. As can be seen from the above results, the concentration profile of NO₂ in the photolysis of NH₄NO₃ on TiO₂ has two peaks and is different from other nitrates. To elucidate the origin of the second NO₂ peak, the concentration profile of NO₂ in the photolysis of NH₄NO₃ on TiO₂ under different conditions is compared in Figure 5A. It was found that the occurrence of the second peak of NO₂ only appears during photolysis in air. When the carries gas was changed to N₂, the second concentration peak of NO₂ disappeared. Combined with the comparison of photolysis of other nitrates (Figure S3), these results suggest that the second NO₂ peak is likely derived from the oxidation of ammonium or ammonia. This is in agreement with the results of Kebede et al.⁸⁸ that the photochemical oxidation of NH₃ on TiO₂ results in the formation of NO and then part of NO could be oxidized to NO₂. The DRIFTS spectrum of TiO₂ exposed to 1 ppm NH₃ upon UV irradiation in Figure 4B shows the formation of nitrate during the oxidation reaction. These surface nitrates could be the intermediates in the photochemical conversion of NH₃ to NO_x . When the carrier gas is N_2 , the absence of O_2 limited the oxidation of ammonium.

To further demonstrate the photo-oxidation of ammonium, in situ DRIFTS was applied to explore the change of the surface species with time in the photolysis process with or without O_2 . The results are shown in Figure 5B. In air stream, several negative peaks at 1614, 1288, and 1247 cm⁻¹ attributed to nitrate⁸⁶ and at 1465 cm⁻¹ attributed to ammonium^{89,90} were observed during the photolysis reaction, indicating that both the surface nitrate and the ammonium were involved. In contrast, in the N₂ stream, the IR bands attributed to nitrate (1614, 1589, 1515, 1492, 1288, and 1248 cm⁻¹) with more negative intensities were observed, which are consistent with the results in Figure 4A. However, the negative peak attributed to ammonium around 1465 cm⁻¹ was not observed, suggesting no oxidation of ammonium. Thus, the oxidation of NH₃ happened in the photolysis of NH₄NO₃ in air on TiO₂.

This result can partly explain that the production rate of NO₂ for NH_4NO_3 is higher than that of other nitrates (Figure 2) because of the contribution of ammonium oxidation to NO₂. Moreover, the consumption of ammonium blocks the recombination of NO₃⁻ with ammonium on the surface, which is different from metal nitrates in that alkali oxides or hydroxides of metals remain on the surface after the photolysis of nitrate. Ammonium is an important chemical to neutralize sulfate and nitrate in the atmosphere. The ratio of the equivalents of ammonium to the sum of sulfate plus nitrate is always close to one in PM_{2.5} samples,⁹¹ indicating that nitrate mainly exists in the form of ammonium nitrate. While in ammonium-poor samples, some metal ions (e.g., Ca²⁺, K⁺, Fe³⁺) in the crystal may be involved in the neutralization of sulfate and nitrate. A previous study showed that the mixed particles of $(NH_4)_2SO_4$ and nitrate finally can form the core-shell structure particles of gypsum wrapped with NH4NO3 after a process of humidification and dehumidification in the atmosphere.⁹² Therefore, nitrate formed in the ammonia-rich area is prone to renoxification.

In summary, it is found that the alkalinity of cation and coexistence of SO_2 and H_2O are important factors affecting the observed production rates of NO_2 and HONO in the photolysis of nitrates on mineral dust containing TiO_2 . NO_3 radicals may be generated in the photolysis of nitrate on TiO_2 and may participate in the oxidation of volatile organic compounds and the formation of secondary organic aerosols. The heterogeneous

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reactions of reactive nitrogen species on mineral dust have been recognized as a significant sink of NO_x and HNO_3 . Consequently, mineral dust mixing with nitrate is ubiquitous in the atmosphere. The average lifetime of mineral dust in the troposphere is about a few days or weeks, which can be transported to thousands of kilometers or more, having an important impact on atmospheric chemistry globally.^{19,50,93,94} When passing through the industrial or urban regions with high NO_x concentration, the heterogeneous reaction on mineral particles leads to their mixing with nitrate. The nitrate aged mineral dust can export NO_r in remote areas with low NO_r concentration through the photolysis renoxification process, which could then affect the regional air quality. The results in the present study indicate that the photolysis of nitrate can be accelerated under complex air pollution conditions with the coexistence of mineral dust and high concentrations of NH₃ and SO₂, for example, in the North China plain.^{70,95,96} Thus, the NO_x migration and transformation accompanied by mineral dust transportation and its impact on regional and global atmospheric environment are worthy of further study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c02182.

Microscope images (Figure S1) and Raman spectra (Figure S2) of TiO₂, NH₄NO₃, and their mixtures; photolysis products of NaNO₃, Ca(NO₃)₂, and Fe(NO₃)₃ on TiO₂ particles (Figure S3); hygroscopic growth factors of Fe(NO₃)₃ (Figure S4); and DRIFTS spectrum of NH₄NO₃-coated TiO₂ particles exposed to SO₂ (Figure S5) (PDF)

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Notes

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