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The nitration of pyrene adsorbed on silica particles by nitrogen dioxide

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Abstract

Conversion of NO_2, HNO_2 gas, their mixture and a mixed gas of HNO_2 and HNO_3 on silica particles was investigated under simulated atmospheric conditions. Both HNO_2 and HNO_3 were detected as the products from conversion of NO_2 on silica particles. However, unlike HNO_3, which increased with conversion time, HNO_2 underwent an increase–decrease time course due to the increased HNO_3 further transformed HNO_2 into NO^+ on silica particles. Considering the catalytic effect of HNO_3 and HNO_2 on the nitration of pyrene adsorbed on silica particles by NO_2, another electrophilic nitration path, analogous to the one that we previously reported, with $NONO_2^+$ and $NON_2O_4^+$ as electrophiles was suggested. The two paths together gave an appropriate explanation for the catalytic effect of HNO_2, HNO_3 and their mixed gas on the nitration of the adsorbed pyrene by NO_2.

Keywords: Polycyclic aromatic hydrocarbons; Pyrene; Heterogeneous nitration; Nitration mechanism; Catalytic effect; Nitrogen dioxide; Nitrous acid; Nitric acid

1. Introduction

Over the past few decades a considerable number of studies have been made on the formation and transformation of polycyclic aromatic hydrocarbons (PAH) in the atmosphere. The reason for the high concern about PAH is not only because of their potential carcinogenicity and mutagenicity (CBEAAP, 1972), but also lies in the fact that many nitro derivatives of PAH are much more effective carcinogens and mutagens than their parent species (Salmeen et al., 1982; Rosenkranz and Mermelstein, 1983; Tokiwa and Ohnishi, 1986). Therefore, the conversion of PAH, especially nitration, in the atmosphere is attracting much more attention. Many less volatile PAH and nitro polycyclic aromatic hydrocarbons (NPAH) have been detected on atmospheric particles (Pitts et al., 1985; Nielsen et al., 1996), this implies that heterogeneous reaction of adsorbed PAH with NO_2 may play an important role in the NPAH formation. For this reason, many attempts have been made by exposure adsorbed PAH to NO_2 (Pitts et al., 1978; Ramdahl et al., 1984; Wu and Niki, 1985; Inazu et al., 1997; Wang et al., 1999) or mixed gases of NO_2 and HNO_3 (Pitts et al., 1978; Wang et al., 1999). We have recently reported that the nitration of pyrene (PY) adsorbed on silica particles by NO_2 is an autocatalyzed reaction. HNO_3 formed from the conversion of NO_2 on silica particles is confirmed as a catalyst, and an electrophilic nitration mechanism has also been given out (Wang et al., 1999).

Our latest research demonstrated that HNO_2 gas also acted catalytically to the nitration of PY adsorbed on silica particles by NO_2. Although HNO_2 was not as

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effective as HNO_3 gas, its catalytic effect could be greatly promoted when mixed with HNO_3, and a synergistic effect was observed (Wang et al., 2000) Considering these facts and the formation of HNO_2 during the nitration process of PY adsorbed on silica particles by NO_2 (Wang et al., 1999), we made a further investigation on the conversion of NO_2, HNO_2 gas, their mixture and a mixed gas of HNO_2 and HNO_3 on silica particles. Based on these experimental results and our previous studies (Wang et al., 1999, 2000), another nitration path, similar to what we have recently presented (Wang et al., 1999), was suggested.

2. Experimental

A fluidized-bed reaction system was used for this study. All experiments were carried out under the condition of room light at room temperature (25 ± 2°C). HNO_3 and HNO_2 formed on silica particles were determined by ion chromatograph. HNO_3 gas was prepared by the reaction of concentrated H_2SO_4 and $NaNO_3$ in an impinger with the aeration of N_2 gas. The above-mentioned experimental conditions have been described in detail previously (Wang et al., 1999).

HNO_2 gas was generated by continuously dripping a solution of 0.002 M $NaNO_2$ into 0.2 M H_2SO_4, while flushing N_2 gas at a flow rate of 200 or 400 ml/min. The concentration of HNO_2 gas in N_2 varied by changing the dripping rate of $NaNO_2$ solution. A more detailed description for the generation method of HNO_2 gas can be obtained in our previous work (Wang et al., 2000).

3. Results and discussion

3.1. Conversion of NO_2 on silica particles

Our recent study (Wang et al., 1999) indicated that the nitration of PY adsorbed on silica particles was an electrophilic reaction, which was assumed to take place in and/or on the water layer adsorbed on silica particles. Besides HNO_3, which was almost linearly increased with time, small amount of HNO_2 was also detected on the PY-adsorbed silica particles during the nitration by NO_2.

A further investigation as shown in Fig. 1 illustrates that the concentrations of HNO_3 formed on silica particles increase with the increasing NO_2 concentrations, while for that of HNO_2, an increase–decrease trend vs. exposure time is apparently revealed. Both HNO_3 and HNO_2 are formed from the conversion of NO_2 via surface reactions, at least the following reactions are believed responsible for the heterogeneous formation of HNO_3 and/or HNO_2 on solid surfaces (Lee and Schwartz, 1981; Sakamaki et al., 1983; Lammel and Perner, 1988; Hotholt et al., 1992; Ammann et al., 1998)

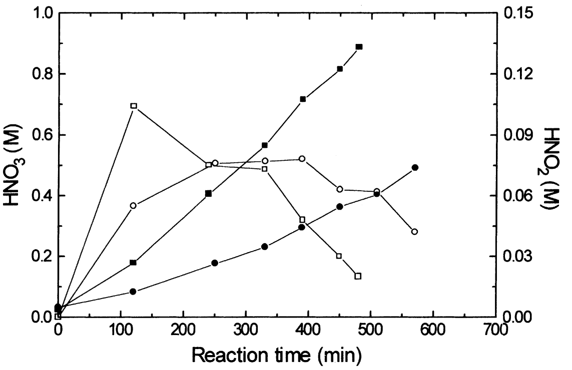


Fig. 1. Concentrations of HNO_3 (black) and HNO_2 (white) formed on silica particles by passing 9.8 ppm (square) or 4.9 ppm (circle) NO_2.

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2 \quad (1)$$

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \quad (2)$$

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \quad (3)$$

$$NO_2 + RED_{ads} \rightleftharpoons HNO_2 + OX_{ads} \quad (4)$$

It is not our aims to go into details about the formation path of HNO_2 and HNO_3 on silica particles. No matter how HNO_2 is formed, the concentration of HNO_2 on silica particles should not be decreased unless some reactions have taken place between HNO_2 and other chemical species on silica particles. If it were the reason of low affinity of HNO_2 to silica particles, the concentration of HNO_2 on silica particles should keep in constant instead of decrease after reached the maximum.

3.2. Conversion of HNO_2 gas and a mixed gas of HNO_2 and NO_2 on silica particles

Fig. 2 displays the variation of HNO_3 and HNO_2 formed on silica particles as a function of passing gases and exposure time. The concentration of HNO_2 converted from HNO_2 gas on silica particles does not increase continuously with the exposure time, it undergoes an increase–decrease course with a maximum concentration of ca. 0.46 M in water adsorbed on silica particles. Small amount of HNO_3 is also detected on silica particles and slowly increases with time. The HNO_3 seems not be formed from the conversion of HNO_2, otherwise, a sharp increment in the concentration of HNO_3 should present correspondingly to the decrease of HNO_2 on silica particles (Fig. 2). Since small amount of NO_2 inevitably exists in prepared HNO_2 gas

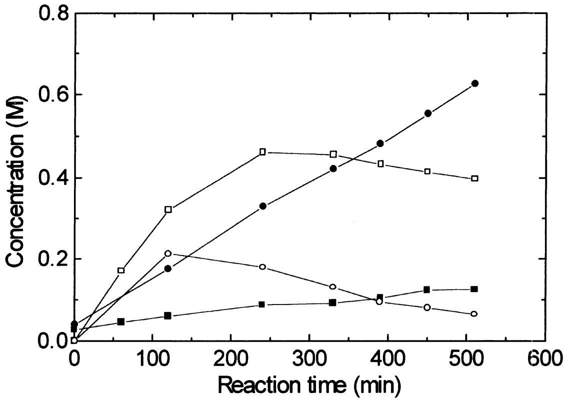


Fig. 2. Concentrations of HNO_3 (black) and HNO_2 (white) formed on silica particles by passing 6 ppm HNO_2 gas (square) or a mixed gas of 6 ppm HNO_2 and 4.9 ppm NO_2 (circle).

(Cox, 1974), the HNO_3 may be formed from the conversion of the NO_2.

In spite of the fact that the conversion of NO_2 on silica particles also leads to the formation of HNO_2 (Fig. 1), the addition of 4.9 ppm NO_2 to 6 ppm HNO_2 gas does not promote the concentration of HNO_2 on silica particles, instead, obviously lowers it. A much clearer increase–decrease curve of HNO_2 on silica particles is also observed. Contrary to HNO_2, the concentration of HNO_3 formed on silica particles is almost linearly increased with time, and is roughly equal to the sum of that separately formed from the conversion of 4.9 ppm NO_2 and 6 ppm HNO_2 gases as shown in Figs. 1 and 2. These results imply that NO_2 and/or its conversion product, HNO_3, may be responsible for the degradation of HNO_2 on silica particles.

3.3. Conversion of a mixed gas of HNO_2 and HNO_3 on silica particles

To further confirm the influence of HNO_3 to the concentration of HNO_2 on silica particles, conversion of a mixed gas of HNO_2 and HNO_3 on silica particles is investigated (Fig. 3), and similar results, just like what we get in Figs. 1 and 2, are observed. This clearly indicates that HNO_3 is the real species caused the declination of HNO_2 on silica particles.

$$HNO_2 + H^+ \rightleftharpoons H_2O + NO^+ \qquad (5)$$

It is known that HNO_2 exists in equilibrium with NO^+ in strong acid via Eq. (5), and the concentration of NO^+ depends on that of acid (Singer and Vamplew, 1956; Bayliss et al., 1963). Eberson and Radner (1980, 1985a) even pointed out that HNO_2 in HNO_3 existed to some extent as NO^+. In view of these facts, it is easy to understand the decrease of HNO_2 with the increasing HNO_3 formed on silica particles as shown in Fig. 1. Although the concentration of HNO_2 on silica particles can up to ca. 0.46 M, the continuously increased HNO_3 obviously led to the equilibrium of Eq. (5) shift to the right and lowered the concentration of HNO_2 on silica particles when exposed to mixed gases of HNO_2 and NO_2 (Fig. 2) or HNO_2 and HNO_3 (Fig. 3), respectively.

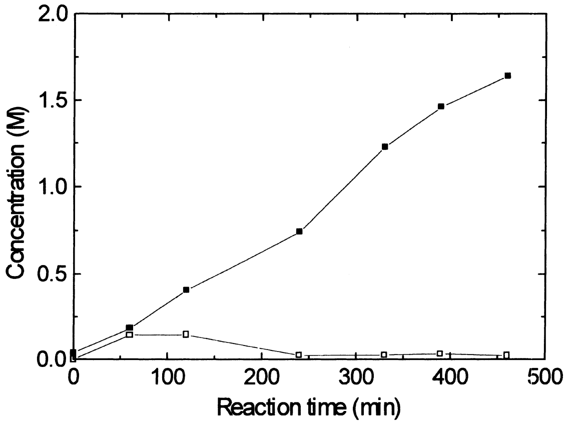


Fig. 3. Concentrations of HNO_3 (■) and HNO_2 (□) formed on silica particles by passing a mixed gas of HNO_2 (6 ppm) and HNO_3 (10) ppm.

3.4. Possible chemical species formed on silica particles

As a weak acid, only a small portion of HNO_2 is anticipated to dissociate into NO_2^- in water adsorbed on silica particles. In addition, the coexistence of HNO_3 with HNO_2 will also turn the equilibrium of Eq. (6) to the left and further lessen the formation of NO_2^-.

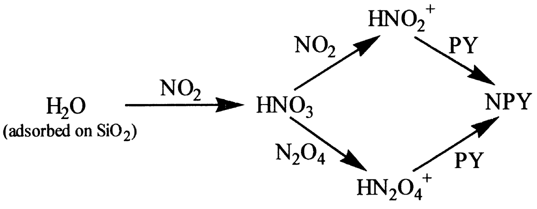
$$HNO_2 \rightleftharpoons H^+ + NO_2^- \qquad (6)$$

Owing to the existence of equilibrium between NO_2 and N_2O_4, minor amount of N_2O_4 is expected to exist by uptake of NO_2 in the liquid phase on aerosols and by adsorption of NO_2 on particle surfaces (Nielsen, 1984). N_2O_4 can further dissociate into NO^+ and NO_3^- in solution following Eq. (7) (Carberry, 1959). Hence, at least the following chemical species, such as H^+, NO_3^-, NO_2, NO^+, N_2O_4 and much less amount of NO_2^-, are possibly existing on the surface of silica particles.

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (7)$$

3.5. Insight into the nitration mechanism of the PY by NO_2

We have reported an electrophilic nitration mechanism (Scheme 1) with HNO_2^+ and $HN_2O_4^+$ as electro-



Scheme 1

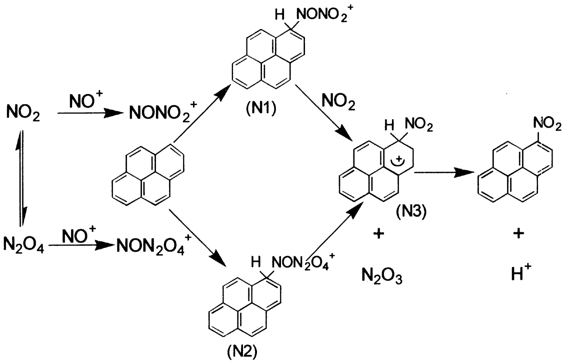
philes (Wang et al., 1999). This mechanism gave a proper explanation for the nitration process of the PY by NO_2 and also the catalytic effect of HNO_3. However, it is insufficient to interpret the phenomenon that the concentration of HNO_2 formed during the nitration process experienced an increase–decrease course (Wang et al., 1999); it is also very difficult to explain the catalytic effect of HNO_2 and the synergistic effect of the mixed gas of HNO_2 and HNO_3 on the nitration of the PY, since the catalytic effect of HNO_2 on the nitration should not be completely ascribed to the trivial amount of HNO_3 detected from the conversion of HNO_2 on silica particles (Wang et al., 2000).

As a precursor of OH radical, HNO_2 is considered to be responsible for the high concentration of OH radical in the early morning (Pitts, 1983; Harrison et al., 1996; Ammann et al., 1998). Nevertheless, under our experimental conditions, the photolysis of HNO_2 is negligible or not happened because the changes on light conditions from room light to dark led to variations of the nitration of the PY neither on rate nor on products (Wang et al., 2000). Therefore, HNO_2 is expected to take part in the nitration via conversion to the other chemical species, such as H^+, NO_2^- or NO^+. Owing to a weak acid, the low ionic dissociation of HNO_2 makes it very difficult to accept the assumption that large amount of H^+ can be formed in the adsorbed water to catalyze the nitration of the PY via Scheme 1.

NO^+ was proved to be a strong oxidant toward PAH, and PAH radical cations were formed in high concentrations by NO^+ for those PAH of redox potential (E^0)$\leqq$1.6 V (Eberson and Radner, 1984). Hence, it seems reasonable to propose that the nitration initiated via electron transfer (ET) from the PY ($E^0 = 1.6$ V) to NO^+, followed by the combination of PY cation with NO_2 or NO_2^- to form nitropyrene as Pryor et al. (1984) suggested. However, these possibilities were completely refused by Eberson and Radner (1980, 1985b) based on their experimental results.

The nitration of the PY was proved to be an electrophilic reaction by comparing the nitration rate of 1-substituted PYs, and also the comparison of their nitration products with the calculated HOMO electron density (Wang et al., 1999). Just like NO_2 and N_2O_4, NO^+ was also a weak electrophile (Eberson and Radner, 1985a). Therefore, under the condition of the coexistence of HNO_3 and HNO_2, both protonation (Ogata and Sawaki, 1966; Effenberger et al., 1974; Eberson and Radner 1985a; Wang et al., 1999) and nitrosation (Goulden and Millen, 1950; Eberson and Radner, 1985a) of NO_2 and N_2O_4 are expected to form more reactive electrophiles. Analogous to Scheme 1, another nitration path is suggested as shown in Scheme 2. $NONO_2^+$ and $NON_2O_4^+$ attack PY on C-1 position possessing the highest electron density to form N1 and N2, whose conversions bring about N3 and further decompose to the final product, 1-nitropyrene. Eberson and Radner (1985a) have reported that the addition of NO^+ salt and strong acid to 0.0005 M shortened the half-life of chrysene nitrated by N_2O_4 in dichloromethane from 65 to 3 and 0.5 min, respectively. On this account, it is reasonable to believe that $NONO_2^+$ and $NON_2O_4^+$ are electrophiles much more effective than HNO_2^+ and $HN_2O_4^+$.

The formation of these electrophiles depends on H^+, NO^+ and NO_2/N_2O_4, while NO^+ is positively correlated with H^+ on silica particles (Eq. (5)). When the PY was nitrated only by NO_2 gas, the formation of these electrophiles depended on both HNO_2 and HNO_3. At the initial stage of the reaction, only small amounts of HNO_3 and HNO_2 were formed from the conversion of NO_2 and much fewer amount of NO^+ was anticipated to generate via Eqs. (5) and (7). These are clearly unfavorable to the formation of electrophiles, and resulted in the long induction period in the nitration process of the PY by NO_2 (Wang et al., 1999). With the lengthening of reaction time, the concentration of HNO_3 clearly increased and led to the formation of HNO_2^+ and $HN_2O_4^+$. Moreover, the increased H^+ inevitably caused the equilibrium of Eq. (5) shift to the right to bring about the decrease in the concentration of HNO_2 on silica particles (Fig. 1), and simultaneously yielded NO^+ to form more reactive electrophiles, $NONO_2^+$ and $NON_2O_4^+$. As a result, the nitration rate of the PY was apparently accelerated (Wang et al., 1999), and the



Scheme 2

concentration of HNO_2 on silica particles experienced an increase–decrease course with time (Fig. 1).

When the nitration of the PY was catalyzed by HNO_2 gas, the formation of electrophiles was also restricted by HNO_3. However, with the increase of HNO_3 formed on silica particles, large amount of electrophiles, especially for $NONO_2^+$ and $NON_2O_4^+$, could be formed as a result of the consumption of HNO_2 via Eq. (5) on silica particles (Fig. 2) and the nitration was apparently accelerated (Wang et al., 2000). In contrast, when the nitration was catalyzed by HNO_3 gas, large amount of electrophiles HNO_2^+ and $HN_2O_4^+$ could be rapidly formed and led to a faster nitration rate than that catalyzed by HNO_2 (Wang et al., 1999, 2000) even though HNO_2^+ and $HN_2O_4^+$ are electrophiles less effective than $NONO_2^+$ and $NON_2O_4^+$. Under the condition that HNO_2 and HNO_3 gases together served as catalysts, all kinds of the electrophiles could be formed in large amount to accelerate the nitration process even at the initial nitration stage. This certainly will lead to the synergistic effect, that is the catalytic effect of the mixed gas of HNO_2 and HNO_3 is more efficient than the sum of that of HNO_2 and HNO_3 when separately used, as what Wang et al. (2000) reported.

4. Conclusions

Both HNO_3 and HNO_2 showed catalytic effects to the nitration of the PY adsorbed on silica particles by NO_2 (Wang et al., 1999, 2000). This work further confirmed the formation of HNO_3 and HNO_2 on silica particles from the conversion of NO_2, and the concentration of HNO_2 experienced an increase–decrease course with time due to the simultaneously formed HNO_3 transformed HNO_2 into NO^+. On account of these facts, another nitration path (Scheme 2), analogous to what we reported previously as show in Scheme 1 (Wang et al., 1999), was suggested for the nitration of the PY. The two schemes together offered proper interpretations for not only the nitration process of the PY by NO_2 and the increase–decrease curve of the concentration of HNO_2 formed, but also the catalytic effects of HNO_2 and HNO_3 gases as well as their mixture.

Both HNO_2 and HNO_3 are easily formed from the conversion of NO_2 on solid surfaces (Lammel and Perner, 1988; Harrison et al., 1996; Ammann et al., 1998; Wang et al., 1999). They were also reported coexisting with NO_2 in the atmosphere, each representing 5–10% of the concentration of NO_2 in southeastern England (Kitto and Harrison, 1992). Therefore, it is reasonable to believe that certain amount of NPAH adsorbed on atmospheric particles could be formed via the nitration paths we suggested (Schemes 1 and 2) under dark or dim light conditions.

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