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Autocatalytic Nitration of Pyrene by Aerated Nitrogen Dioxide in Solution and Comparison with the Nitration on Silica Particles

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The nitration mechanism of pyrene (PYH) by aerating NO_2 in solution was studied by varying the factors (concentration of NO_2, addition of HNO_3 gas and H_2O, 1-substituent on PYH, and solvent) affecting the nitration. Only 1-nitropyrene was formed. In acetonitrile, both the decrease in PYH and the increase in 1-nitropyrene depicted sigmoid curves, that is, their changes proceeded abruptly after an induction period, and finally approached to zero. The characteristic feature was reasonably explained by the facts that H^+ dissociated from HNO_3, accumulated by aerating NO_2 into trace water-containing acetonitrile and released by the nitration, acted as an autocatalyst. The nitration proceeded electrophilically based on the 1-substituent effect of PYH, and accelerated with increasing polarity of the solvents. The nitration was studied kinetically and an ionic mechanism involving NO_2^+ as an electrophile was proposed. The nitration mechanism of PYH in acetonitrile was different from that in the adsorbed water on silica gel.

Most of the nitration of an aromatic ring has been carried out in strongly acidic, polar media, and under these conditions the nitrating species is generally regarded as a nitryl cation.[1] Although less frequently discussed in textbooks, nitration can also be carried out by NO_2/N_2O_4 in organic solutions.[2–10] Despite the numerous studies devoted to the nitration of polycyclic aromatic hydrocarbons (PAH), the nitration of PAH with NO_2/N_2O_4 is fairly complex[3] and often controversial.[5,7] Hitherto, free-radical attack,[5,6] ionic electrophilic substitution,[3–5,7] electron-transfer (ET),[2,8,9] and nitrosation[10] mechanisms have been proposed. The operating reaction mechanisms depend upon the substrates,[2] solvent polarity,[5–7] temperature,[7] and the existence of an acid[6,7] and water.[7]

The nitration of PAH using NO_2/N_2O_4 is very mild, but not explored fully for synthetic purposes. It is especially useful for easily oxidizable aromatics and is more selective than NO_2^+ effected ones.[4] Furthermore, it does not require a subsequent strong acid work-up. The nitration of PAH in polar solvents is known to be catalyzed by the addition of protons[3,6,7] and Lewis acids,[7] however, the rate is slow for nonactivated aromatic compounds, such as benzene, naphthalene, and triphenylene.[2,11] Suzuki et al.[12] have reported that the nitration of nonactivated arenes can be promoted by the addition of O_3 to N_2O_4 in polar and nonpolar solvents, and is more accelerated by the addition of protons and Lewis acids. Compared with the nitration of PAH by NO_2/N_2O_4 and O_3-added NO_2/N_2O_4 in solution, none has been reported concerning the nitration process, kinetics, and mechanism when NO_2 is aerated in a solution containing PAH.

On the other hand, the reaction between PAH and NO_2 has received considerable interest as a possible route to the formation of mutagenic nitro-polycyclic aromatic hydrocarbons (NPAH) in the gas phase and on suspended particulate matters (SPM) in the atmosphere.[13–15] Nielsen[11] investigated the nitration rates of 25 PAHs in water–methanol–dioxane containing N_2O_4, HNO_3 (excess), and HNO_2 under conditions which are relevant for determining the relative reactivity of PAH toward nitrogen compounds in the atmosphere, and noted that nitration follows a pseudo first-order kinetics to the concentration of PAH. The aeration of gaseous nitrating species, such as NO_2, HNO_3, and HNO_2, on PAH adsorbed on SPM is an important model for elucidating the nitration process of PAH in the atmosphere. Using a simulation apparatus, we have recently reported that the nitration of pyrene (PYH) adsorbed on silica particles proceeds autocatalytically and electrophilically.[16–18] These behaviors were reasonably explained by the facts that dissociated H^+ of HNO_3, accumulated by the reaction of NO_2 with the adsorbed water on silica particles, acts as an autocatalyst, and the resultant $HNO_2^{\bullet+}/HN_2O_4^+$ attacks at carbon atoms having a high electron density. It is reasonable to assume that adsorbed water forms a water layer on the surface of silica particles, and that a micro solution environment is prepared for nitration. Thus, the nitration can be considered to be a reaction occurs in the water layer. Considering these facts, it is expected that the H^+-catalyzed nitration of PAH with NO_2 can also occur in organic solutions containing trace water. Actually, a similar nitration path was observed between in solution and on silica particles.

This paper describes the nitration of PYH by NO_2 in acetonitrile, factors (concentration of NO_2, addition of HNO_3 gas and H_2O, 1-substituent on PYH, and solvent) affecting the nitration, chemical species formed during the nitration, kinetics, and mechanism. The results are compared with the nitration of PYH on silica particles.

Experimental

Materials. PYH and 1-nitropyrene (1-NO_2PY) were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. 1-Methylpyrene (1-MePY),[16] 1-methoxypyrene (1-MeOPY),[17] and 1-bromopyrene (1-BrPY)[18] were synthesized

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by the reported methods. Solvents of acetonitrile, methanol, chloroform, and dichloromethane were used as purchased from Wako Pure Chemical Industries, Ltd. The water content of acetonitrile was varied by adding water to acetonitrile with a microsyringe.

A cylinder-loaded NO_2 gas (100 ppm in N_2) was supplied by Takachiho Chemical Industry Inc. NO_2 gas of various concentrations was prepared by mixing certified NO_2 gas with N_2 gas with a flow meter. A Saltzman solution determining the concentrations of NO_2 and NO was prepared according to the reported method.[19] HNO_3 gas (10.3 ppm) was generated by aerating N_2 gas at a flow rate of 400 mL $\min^{-1}$ through an impinger containing 10 mL of concentrated H_2SO_4 and 0.8 g of $NaNO_3$ at 25 °C.

Conversion of NO_2 in Acetonitrile. NO_2 (100 ppm) was passed through an impinger containing acetonitrile (20 mL) at a flow rate of 400 mL $\min^{-1}$ and the chemical species in the solution and the effluent gas were determined. First, the species were determined by 2 minutes passing at a set time, and their material balance was examined. Second, the concentration change of the species with time was examined. In both experiments, NO_2 and NO in the solution were ejected by passing N_2 through the solutions, and their concentrations were measured by the Saltzman method.[19] On the other hand, after 0.2 mL of the sampled solution was diluted with 1.8 mL of ion-exchanged water, the concentrations of NO_3^- and NO_2^- were measured with ion chromatography (IC). UV–vis and Raman spectra of the nitrogenous species formed by aerating NO_2 in acetonitrile were also measured.

Nitration of Pyrene by NO_2. NO_2 of various concentrations was passed through an impinger containing an acetonitrile solution of PYH (5.00 mg in 20 mL = 1.24 mmol dm^{-3}) at a flow rate of 400 mL $\min^{-1}$ at 11 °C. To supply the decrease in the acetonitrile solution, a small amount of acetonitrile was added occasionally. The solution (0.1 mL) was withdrawn with a microsyringe at timed intervals and diluted to 5 mL with acetonitrile; the decay of PYH (C_t/C_0) was then measured with HPLC at $\lambda = 234$ nm. The nitration of 1-substituted PYH was also performed by a method similar to that of PYH. The products were measured with GC/MS after concentration of the solution.

Effect of HNO_3 and HNO_2 Gases, Water, Solvent, and 1-Substituent of PYH on the Nitration. The effect of previous aeration of HNO_3 and HNO_2 gases, water addition, and 1-substituent of PYH on the nitration was examined in acetonitrile (20 mL), and the solvent effect was also studied by varying the solvent. HNO_3[16] and HNO_2[17] gases were generated by the same methods as those described previously. After a fixed amount of water and HNO_3 (10.3 ppm) and HNO_2 (11.1 ppm) gases had been added separately, PYH was nitrated with NO_2 (100 ppm) by the same method as that described above.

Analysis. HPLC was performed by a JASCO HPLC system equipped with a PU-980 pump, a 970 UV–vis detector, and a Mightysil RP-18 column. A mixture of $CH_3CN:H_2O = 75:25$ was used as a mobile phase. The structures of the products were examined with a GC/MS (JEOL 700 Q) equipped with a fused-silica capillary column (HP-5, 30 m long, 0.32 mm i.d.). The column temperature was raised from 130 °C to 270 °C at 5 °C $\min^{-1}$. IC of NO_3^- and NO_2^- was performed by a JASCO HPLC system equipped with a Shodex CD-5 electron conductivity detector and a TSK Anion-PW column (eluent: IC-Anion-A). The water content in acetonitrile was measured with a Karl-Fisher meter (Kyoto Electronics, MKC-510N). Electric conductivity was measured with a HORIBA D24 electrode. The UV–vis spectrum was taken on a SHIMADZU 1600 and Raman spectrum on a JASCO micro-Raman spectroscope (NRS-1000, Ar laser, excited at 514.5 nm).

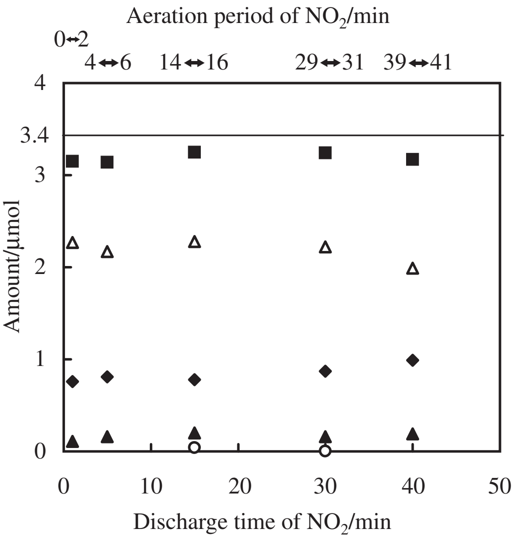


Fig. 1. Conversion products of NO_2 in acetonitrile and their material balance. △: $HNO_3 + HNO_2$, ◆: NO_2(Insoluble), ▲: NO(Insoluble), ○: NO_2 + NO(Soluble), ■: Total, $[NO_2] = 100$ ppm.

Results

Conversion Products of NO_2 and Material Balance. Figure 1 shows the conversion products of NO_2 in acetonitrile and their material balance. The aeration time was each 2 minutes during the discharge of NO_2 (100 ppm). The quantity of NO_2 was calculated to be 3.4 µmol for 2-minute aeration. NO_2 was converted into HNO_3, HNO_2, and NO by a reaction with trace water (447 ppm) in acetonitrile according to, at least, the following three reactions,[20,21] which are well known to occur when NO_2 was absorbed in water:

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2, \tag{1}$$

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO, \tag{2}$$

$$NO_2 + NO + H_2O \rightleftharpoons 2HNO_2. \tag{3}$$

The electric conductivity of HNO_3 was measured after aerating HNO_3 gas (28 ppm) separately in trace water-containing acetonitrile (20 mL) and water (20 mL) for 30 min at a flow rate of 400 mL $\min^{-1}$. The conductivity was estimated to be 3.34 mS m^{-1} for acetonitrile and 82.0 mS m^{-1} for water at 25 °C.This result shows that HNO_3 formed was partially dissociated in polar acetonitrile and could afford H^+ continuously as it was consumed.

Since each sampled aliquot was diluted with water before an IC measurement, the molar amounts of NO_3^- and NO_2^- can be regarded as being the same as those of HNO_3 and HNO_2, respectively. The total molar amount of HNO_3 and HNO_2 is larger than each molar amount of NO_2 and NO in the effluent gas, while the total molar amount of NO_2 and NO in acetonitrile is much smaller than each molar amount of NO_2 and NO in the effluent gas. The material balance is fairly good between the amount of NO_2 (3.4 µmol) in the influent gas and the total amount of HNO_3, HNO_2, NO_2, and NO in acetonitrile and the effluent gas.

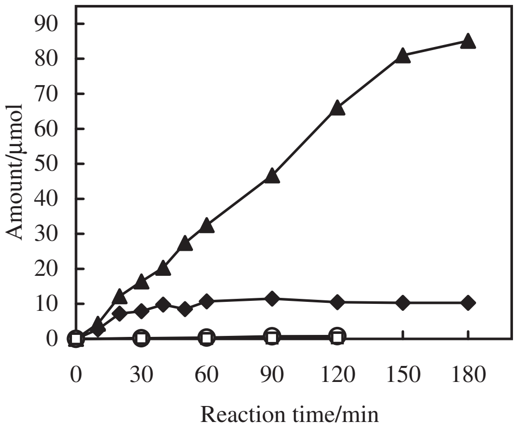


Fig. 2. Change in the conversion products of NO_2 with aeration time in acetonitrile. ▲: HNO_3, ◆: HNO_2, ○: NO_2, □: NO, $[NO_2] = 100$ ppm.

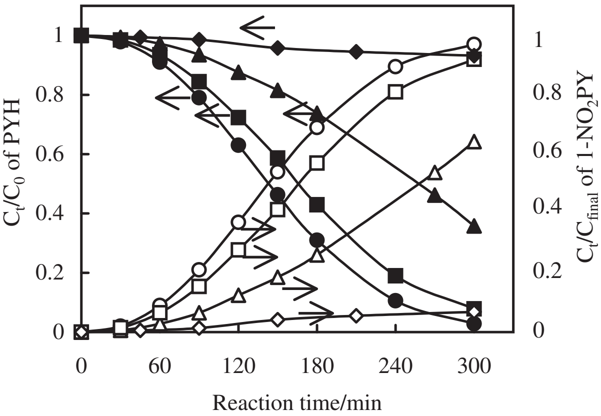


Fig. 3. Effect of NO_2 concentration on the decay of PYH and on the increase in 1-NO_2PY with time. [PYH] $= 1.24$ mmol dm^{-3}, $[NO_2]$/ppm: ◆, ◇: 10, ▲, △: 50, ■, □: 75, ●, ○: 100, PYH: Black, 1-NO_2PY: White.

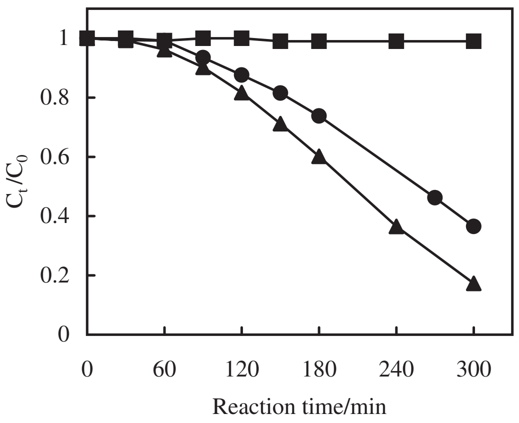


Fig. 4. Effect of added HNO_3 gas on the decay of PYH by NO_2. [PYH] $= 1.24$ mmol dm^{-3}, ■: HNO_3 (49 ppm), ●: NO_2 (50 ppm), ▲: NO_2 (50 ppm) + HNO_3 (5 ppm).

Figure 2 shows the change in the conversion products of NO_2 in acetonitrile with aeration time. The molar amount of each product increases in the order: $HNO_3 > HNO_2 \gg NO_2 > NO$. The amount of HNO_3 increases linearly with time, and the increase becomes slow after 150 minutes, while that of HNO_2 reaches at a constant at 60 minutes. On the other hand, the molar amount of NO_2 and NO increases with time, and is saturated after about 20 minutes. Hayashi et al.[20] reported that the exposure of a NO_2–NO–N_2 gas to distilled water rapidly increased the concentrations of $NO_3{}^-$ and $NO_2{}^-$, and was followed by a slow increase in their concentrations with time.

Nitration of Pyrene by NO_2. The nitration product of PYH was only 1-NO_2PY by HPLC and GC/MS measurements. Figure 3 shows the decay of PYH and the increase in 1-NO_2PY with time by varying the concentration of NO_2. The increase in the concentration of NO_2 increases the decay rate. As obviously shown when NO_2 of more than 75 ppm is aerated, the variation depicts sigmoid curves. At the initial stage, the decay increases slowly, then abruptly increases and finally slowly approaches to zero. The initial decay rate increases with the increasing concentration of NO_2, whereas at the rapid decay stage the decay curves become nearly parallel regardless of the concentration of NO_2. An attractive point is that there is an induction period, which is shortened with the increasing concentration of NO_2. The increase in 1-NO_2PY also depicts sigmoid curves, which are opposite to the decay curves of PYH.

As already shown in Fig. 2, HNO_3 is accumulated linearly in acetonitrile with the aeration of NO_2. It is expected that the HNO_3 acts as a catalyst and accelerates the nitration of PYH by NO_2. The catalytic effect of acids has been reported in the reaction of PAH with N_2O_4 previously added to dichloromethane,[3,6,7] however, nothing has been mentioned about the autocatalytic behavior.

Effect of HNO_3 on the Nitration of Pyrene. Figure 4 shows the effect of added HNO_3 gas on the decay of PYH by NO_2. The decay rate increases by the addition of HNO_3 gas. The aeration of only HNO_3 gas (49 ppm) gave only 0.9% of 1-NO_2PY after 300 minutes. These results give a clear demonstration that HNO_3 never serves as a nitrating species, but a catalyst. The increase in the decay rate can be explained by the increased accumulation of HNO_3 in acetonitrile by the addition of HNO_3 gas.

Furthermore, to make sure the catalytic effect of HNO_3 on the nitration of PYH, we previously aerated HNO_3 gas (10.3 ppm) into acetonitrile and then reacted with NO_2 (100 ppm). Figure 5a shows the effect of the previous aeration time of HNO_3 gas on the decay of PYH by NO_2. The ratio (c/a) of the initial concentration of HNO_3 (c mol dm^{-3}) to PYH (a mol dm^{-3}) is given for each curve. The decay rate increases with increasing the initial concentration of HNO_3. The decay plots express the sigmoid curves, which are characteristic features of autocatalytic reactions.[22–25] The decay rate rapidly increases after the induction period, which is shortened as the initial concentration of HNO_3 increases. A unique feature of this kinetic behavior is that the decay rate exhibits a maximum (r_{max}) along the reaction coordinate (Fig. 5b), which corresponds to the rate at the inflection point of the sigmoid curve. The autocatalytic decay profile of PYH is similar to the profiles of the HNO_2-autocatalyzed oxidation of ferroin by $NO_3{}^-$ in acidic media[23] and the chlorine–thiourea reaction in acidic media,[24] and the nitration of halogen- and carboxyl-substituted benzenes by N_2O_5 in aprotic solvents.[25]

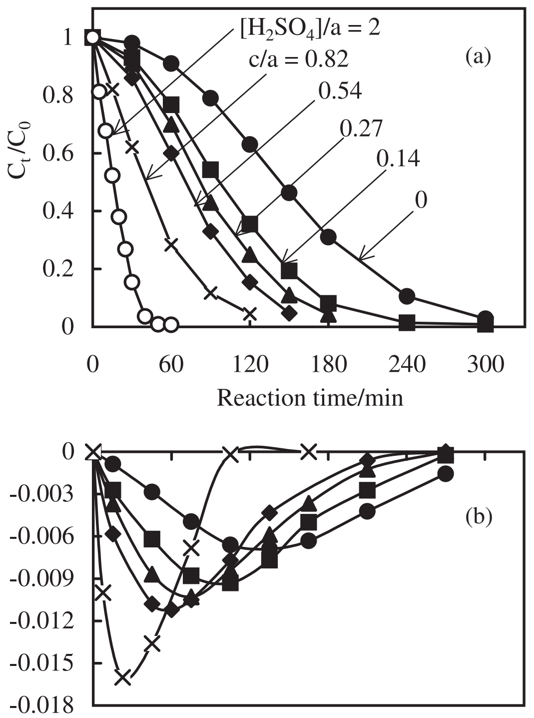


Fig. 5. Effect of previous aeration time of HNO_3 gas and addition of H_2SO_4 in place of HNO_3 gas on the decay of PYH by NO_2. ●: 0 min, ■: 20 min, ▲: 40 min, ◆: 80 min, ×: 120 min, ○: H_2SO_4 (2.48 $mmol\,dm^{-3}$), [PYH] = 1.24 $mmol\,dm^{-3}$, $[NO_2] = 100$ ppm, $[HNO_3] = 10.3$ ppm.

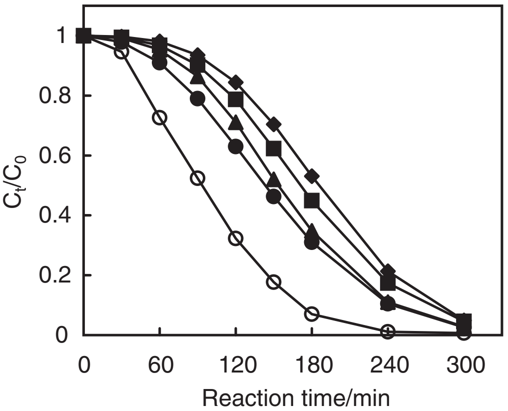


Fig. 6. Addition effect of water to acetonitrile on the nitration of PYH by NO_2. Water content/ppm: ◆: 4200, ■: 3000, ▲: 1500, ●: 447, ○: 180, [PYH] = 1.24 $mmol\,dm^{-3}$, $[NO_2] = 100$ ppm.

Figure 5a also shows the addition effect of concentrated sulfuric acid on the decay of PYH. PYH did not decrease exponentially with time, even when an excess amount of H_2SO_4 ($[H_2SO_4]/a = 2$), stronger acid than HNO_3, was used. Millen[26] reported that N_2O_4 in concentrated sulfuric acid was ionized to produce $NO_2{}^+$ and NO^+ ions.

Effect of Water on Nitration. Figure 6 shows the addition effect of water to acetonitrile on the nitration of PYH. Commercially available acetonitrile was found to contain 447 ppm water. The water content was varied from 180 ppm to 4200 ppm. All of the decay plots express the sigmoid curves, and the decay rate decreases with increasing water content.

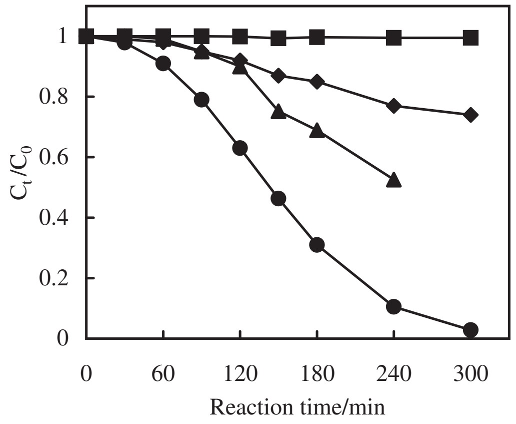


Fig. 7. Solvent effect on the nitration of PYH by NO_2. ●: CH_3CN, ▲: CH_3OH, ◆: CH_2Cl_2, ■: $CHCl_3$, [PYH] = 1.24 $mmol\,dm^{-3}$, $[NO_2] = 100$ ppm.

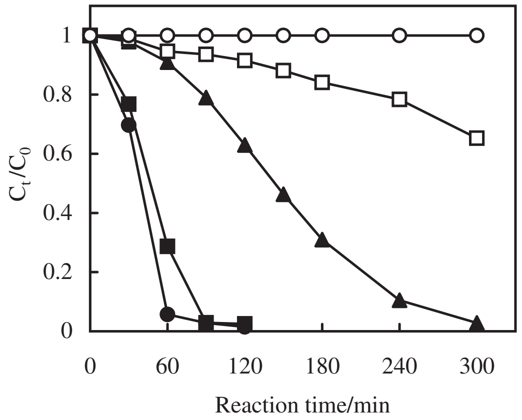


Fig. 8. Substituent effect on the nitration of PYH by NO_2. ●: 1-MeOPY, ■: 1-MePY, ▲: PYH, □: 1-BrPY, ○: 1-NO_2PY, [PYH] = 1.24 $mmol\,dm^{-3}$, $[NO_2] = 100$ ppm.

Effect of the Solvent on Nitration. Figure 7 shows the solvent effect on the nitration of PYH. The decay rate increases with increasing the dielectric constants ($\mathcal{E}$) of the solvents: CH_3CN (37.5) > CH_3OH (32.6) > CH_2Cl_2 (7.77) > $CHCl_3$ (4.8). In a hydrophilic CH_3OH solvent as well as CH_3CN, nitration was accelerated via the induction period, whereas nitration did not substantially occur (1-NO_2PY = 0.5% at 300 min) in hydrophobic $CHCl_3$, although it contained water to react with aerated NO_2. These results can be explained by the fact that in $CHCl_3$ having a much lower dielectric constant than CH_3CN, CH_3OH, and CH_2Cl_2 the dissociation of the accumulated HNO_3 is prevented. The solvent and the HNO_3-catalyzed effects expect that an ionic electrophilic nitration mechanism is more probable than a radical nitration mechanism.[5–7]

Effect of 1-Substituents of Pyrene on Nitration. The nitratin of 1-substituted PYH by NO_2 was also investigated under the same conditions as those of PYH. Figure 8 shows that the decay plots for PY, 1-MePY and 1-MeOPY express the sigmoid curves, except for the slow decay of 1-NO_2PY and 1-

BrPY. The decay rate increases in the order: 1-MeOPY > 1-MePY > PYH > 1-BrPY > 1-NO_2PY. This result shows that the electron-donating groups promote the nitration rate, whereas the electron-withdrawing groups retard it. The substituent effect is a typical feature for an electrophilic reaction, such as an NO_2^+ attack on substituted benzene. From a GC–MS measurement, two mono nitro derivatives were obtained from 1-MeOPY and three nitro derivatives were formed from 1-MePY and 1-BrPY. Although we could not determine the substituted position of a nitro group because of the lack of authentic chemicals and also the difficult separation of the isomers by TLC, the nitration positions for 1-MePY and 1-BrPY were estimated to be 3, 6, and 8, but for 1-MeOPY, only the positions of 6 and 8 were expected to be possible from a calculation of the HOMO electron density of carbon atoms of 1-substituted pyrenes using the LCAO method.

Discussion

Proton Autocatalyzed Nitration of Pyrene. A reaction is autocatalytic if one of its products increases the rate of the reaction.[23] For example, an autocatalyst can accelerate its own production. In this case, some product must be initially present, since otherwise the reaction will never start. In the nitration of PYH by NO_2, although H^+ is not present initially, H^+ that was formed by the dissociation of HNO_3 accumulated by aerating NO_2 (path A) starts the reaction and accelerates the nitration by collaborating with the H^+ that was released with the formation of 1-NO_2PY (path B). The previous aeration of HNO_3 gas (path C) shortens the induction period. Accordingly, the proton autocatalyzed nitration of PYH can be expressed as follows:

$$\mathrm{PYH} + \mathrm{NO_2} \xrightarrow[\text{Paths A, B, and C}]{H^+} \mathrm{PY{-}NO_2} + H^+. \tag{4}$$

Before considering the nitration kinetics of PYH, the amount of HNO_3 accumulated with time was estimated. Figure 9 shows the time course of the amount of HNO_3 accumulated by paths A, B, and C. The amount of HNO_3 via paths A and C increases linearly, whereas that via path B increases sigmoidally. The formation rate of HNO_3 increases in the order: path A > path C > path B and that via path A is 3.2-times larger than that of path C.

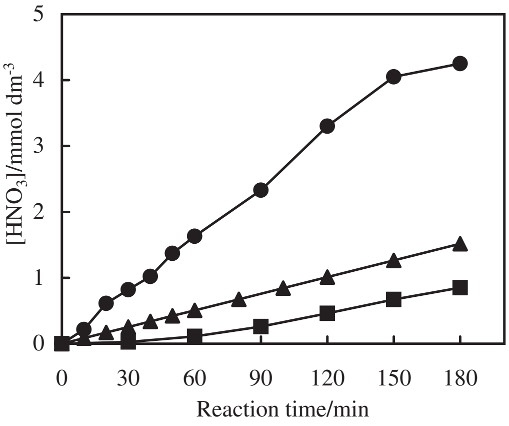


Fig. 9. Time course of the concentration of HNO_3 formed by Paths A, B, and C. ●: Path A, ■: Path B, ▲: Path C, Path A: $[NO_2]$ = 100 ppm, Path B: [PYH] = 1.24 mmol dm^{-3}, $[NO_2]$ = 100 ppm, Path C: $[HNO_3]$ = 10.3 ppm.

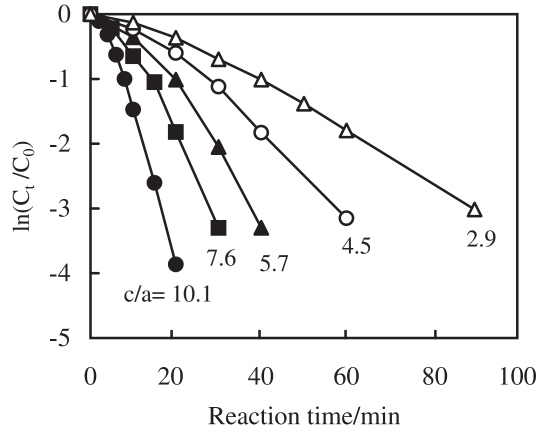


Fig. 10. Plot of $\ln(C_t/C_0)$ versus time for the nitration of PYH by NO_2 in the presence of excess HNO_3. [PYH] = 1.24 mmol dm^{-3}, $[NO_2]$ = 100 ppm, $[HNO_3]$ = 3.6–12.5 mmol dm^{-3}.

Kinetics. As qualitatively shown in Figs. 3 and 5, increasing the concentration of either NO_2 or HNO_3 increases the decay rate of PYH, namely the formation rate of 1-NO_2PY. However, a regular determination of the partial kinetic order with the reactants is not possible under the sigmoid decay of PYH. To simplify the kinetics, the effect of the reactants on the rate was investigated under an excess of one reactant, that is, under a pseudo zero-order condition. Figure 10 shows a plot of $\ln(C_t/C_0)$ versus the reaction time for the nitration of PYH by NO_2 in the presence of excess HNO_3. Even in the case of using 10.1-times HNO_3 to PYH, a short induction period is observed. All of the decay curves obey a linear relationship between $\ln(C_t/C_0)$ and the reaction time after the induction period. This result suggests that after an excess amount of the nitrating species was accumulated by aerating NO_2, PAH decayed according to first-order kinetics under aerating NO_2. Next, to elucidate the order of H^+, the initial concentration of excess HNO_3 was varied, and then the relation between k_{obs} and the concentration of HNO_3 was examined after the induction period. As shown in Fig. 11, a linear relationship having slope k is found, also suggesting first order for H^+. Furthermore, as shown in Fig. 3, the decay of PYH is almost irrespective of the concentration of NO_2 after the induction period.

Therefore, after the induction period the decay rate of PYH can be expressed as

$$-\mathrm{d}x/\mathrm{d}t = k[\mathrm{PYH}][H^+] = k(a-x)(c+x+y), \tag{5}$$

where a is the initial concentration of PYH, x is the concentration of PYH that has reacted after t minutes, y is the concentration of H^+ that has accumulated by the aeration of NO_2 for t minutes, and c is the concentration of H^+ that is present by the previous aeration of HNO_3. When HNO_3 gas is not previously aerated, c may be set as zero in Eq. 5. When c is smaller than a, the decay rate slowly increases, and ultimately $c+x+y$ can be approximated by $x+y$ as $x+y$ increases beyond c. Eq. 5 is expressed as

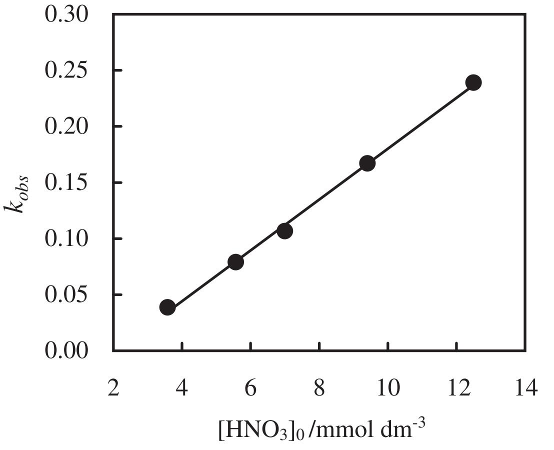


Fig. 11. Plot of k_{obs} versus initial concentration of HNO_3. [PYH] = 1.24 mmol dm^{-3}, $[HNO_3]_0$ = 3.6–12.5 mmol dm^{-3}.

$$-\,dx/dt = k(a - x)(x + y). \tag{6}$$

The decay rate becomes independent of c. We can reasonably explain that the shapes of four curves in Fig. 5a ($c/a = 0$, 0.14, 0.27, 0.54, and 0.82) are similar, except for the induction period.

An attempt to estimate each inflection point (x_c) by differentiating Eq. 5 was unsuccessful because x_c ($x_c = (a - c - y)/2$) involves y, which is a function of t. Alternatively, x_c was estimated from the value of C_t/C_0, which corresponds to $(a - x)/a$, showing the r_{max} of each curve in Fig. 5b. Next, the induction period (t_i) of PYH was estimated by drawing a line tangent to each curve at x_c. Then, the total concentration of HNO_3 ($c + x_i + y_i$) at the induction periods was evaluated from Fig. 9. As summarized in Table 1, it is found that the decay of PYH is accelerated when $c + x_i + y_i$ attained the initial concentration of PYH, a. In the HNO_2-autocatalyzed oxidation of ferroin by NO_3^- in acidic media,[23] it has been reported that if the initial concentration of HNO_2 is compatible with that of ferroin, the autocatalytic behavior disappears.

Eberson et al.[3] studied the relative reactivity of six PAH with N_2O_4 in the presence or absence of a catalytic amount of methanesulfonic acid in CH_2Cl_2, and noted that the increase in the yield of NPAH obeyed approximately a second-order kinetics in the absence of the acid. Nielsen[11] reported that the nitration of PAH with N_2O_4 in excess of HNO_3 follows a pseudo first-order kinetics to the concentration of PAH. The kinetics of the autocatalytic nitration of PYH is different from those suggested by Eberson[3] et al. and Nielsen.[11] This result would arise mainly from the difference of previously added N_2O_4 and aerated NO_2.

Nitration Mechanism. Before discussing a nitration mechanism, the nitrogenous species formed by aerating NO_2 in acetonitrile was examined spectrophotometrically. Figure 12

Table 1. Effect of HNO_3 Formed by Paths A, B, and C on the Nitration of PYH

PYH	HNO_3					HNO_3/mmol dm^{-3}			
a/mmol dm^{-3}	aeration time/min	c/mmol dm^{-3}	c/a	x_c[a]/mmol dm^{-3}	t_i[b]/min	x_i[d]	y_i[c]	$c + x_i + y_i$	$(c + x_i + y_i)/a$
1.24	0	0	0	0.48	47	0.060	1.25	1.31	1.06
1.24	20	0.169	0.14	0.46	35	0.040	0.96	1.17	0.95
1.24	40	0.337	0.27	0.45	28	0.024	0.80	1.16	0.94
1.24	80	0.674	0.54	0.42	18	0.016	0.50	1.19	0.96
1.24	120	1.011	0.82	0.40	8	0.007	0.21	1.23	0.99

a) Concentration of PYH at inflection point. b) Induction period. c) and d) Concentration of HNO_3 formed by Paths A and B at induction period, respectively.

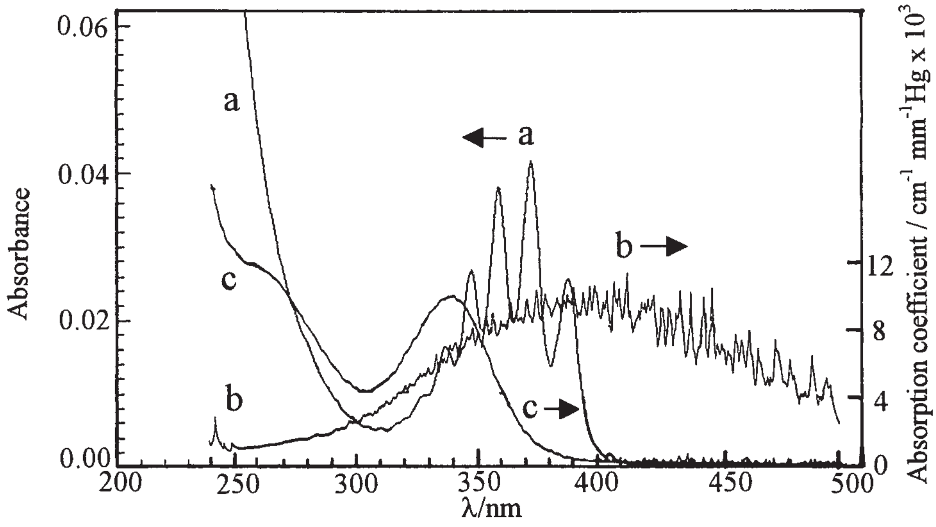


Fig. 12. UV–vis spectra of the nitrogenous species (curve a) formed by aerating NO_2 in acetonitrile together with those of NO_2 (curve b) and N_2O_4 (curve c). [NO_2] = 100 ppm, aeration time = 60 min.

shows the UV–vis spectra of the nitrogenous species (curve a) together with those of NO_2[27,28] ($\lambda_{max} = 410$ nm, curve b) and N_2O_4[27] ($\lambda_{max} = 340$ nm, curve c). In hexane, NO_2 also represented the same absorption maximum at 410 nm and an equilibrium mixture of NO_2 and N_2O_4 represented an isosbestic point at 357 nm.[29] Fine structure appears in the spectrum of NO_2, whereas no fine structure appears in the spectrum of N_2O_4.[27–29] The spectrum of the nitrogenous species shows fine structure ($\lambda = 337$, 347, 358, 372, and 388 nm) at wavelengths slightly longer than that of N_2O_4 ($\lambda_{max} = 340$ nm) and no absorption due to NO_2. Aeration of NO_2 (100 ppm) in acetonitrile (2.48 $mmol\,dm^{-3}$) added concentrated sulfuric acid gave the same spectrum as curve a. The addition of concentrated nitric acid (1.24 $mmol\,dm^{-3}$) to concentrated sulfuric acid (2.48 $mmol\,dm^{-3}$) in acetonitrile, in which NO_2^+ should be formed, gave no absorption at wavelengths longer than 320 nm, showing that the observed fine structure is not due to NO_2^+. Based on these results, it seems reasonable that the species are composed of $H^+N_2O_4$,[3,30] which is in equilibrium with N_2O_4 under acidic condition, and its dissociation product, NO_2^+, although the existence was not proved by Raman spectral measurement[26,31] because a line due to NO_2^+ ($\nu_{N\text{–}O} = 1400$ cm^{-1}) overlapped with a strong line (1390 cm^{-1}) due to acetonitrile. Figure 13 depicts the change in the absorbance at 372 nm with the aeration time of NO_2 under the addition and no addition of H_2SO_4. The concentration of $H^+N_2O_4$ gradually increases with time, and saturates in both cases, showing that the formation rate of $H^+N_2O_4$ is controlled by the amount of aerated NO_2. This result supports that after trace water in acetonitrile is consumed by aerated NO_2, NO_2 is rapidly dimerized,[29,32] and the concentration of $H^+N_2O_4$ is accumulated to reach a nearly stationary state.

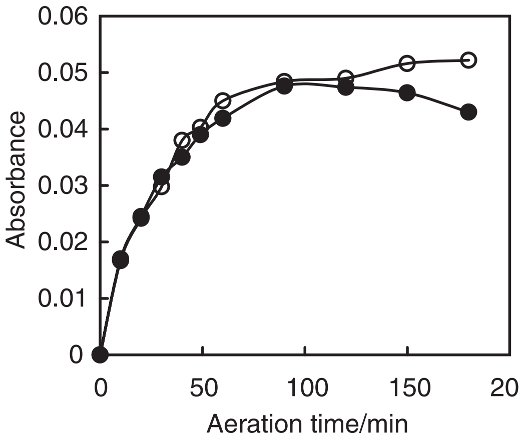


Fig. 13. Change in the absorbance at 372 nm with aeration time of NO_2 under addition (○) and no addition (●) of H_2SO_4. $[NO_2] = 100$ ppm, acetonitrile = 20 mL.

Previous proposals concerning the mechanism of the N_2O_4 nitration of reactive aromatics (ArH) include NO_2^+ or $H^+N_2O_4$ mediated nitration in strongly acidic media[3,30,33–35] (Eqs. 7 and 8), where NO_2^+ is formed through the equilibrium of Eq. 7:

$$H^+ + N_2O_4 \rightleftharpoons H^+N_2O_4 \rightleftharpoons NO_2^+ + HNO_2, \tag{7}$$

$$\begin{aligned} ArH + H^+N_2O_4 &\rightarrow Ar\ NO_2 + H^+ + HNO_2, \\ ArH + NO_2^+ &\rightarrow ArNO_2 + H^+. \end{aligned} \tag{8}$$

To confirm the effect of HNO_2 on the formation of PYH, the nitration of PYH by NO_2 was performed in acetonitrile separately aerated HNO_2 gas (11.1 ppm) and added urea (2.48 $mmol\,dm^{-3}$) as a HNO_2 removing reagent.[30] As shown in Fig. 14, the decay rate of PYH decreased with increasing concentration of HNO_2, and slightly increased as HNO_2 was removed, showing that HNO_2 functions in the equilibrium illustrated in Eq. 7. Since N_2O_4 is too weak an electrophile,[3] protonation is expected to form a much more effective electrophilic attacking species,[3,34,35] $H^+N_2O_4$, for PYH. The effect of water on the decay of PYH (Fig. 6) can be explained by the idea that the formed HNO_3 is diluted with excess water to decrease the concentration of H^+, and eventually to suppress the formation of $H^+N_2O_4$.

Two possible nitration mechanisms are suggested in Scheme 1. An electrophilic attack of NO_2^+ or $H^+N_2O_4$ on the C-1 position of PYH forms a σ-complex, followed by the formation of 1-NO_2PY along with releasing H^+. The H^+ acts as an autocatalyst. Eberson et al.[34] reported that at the low acid

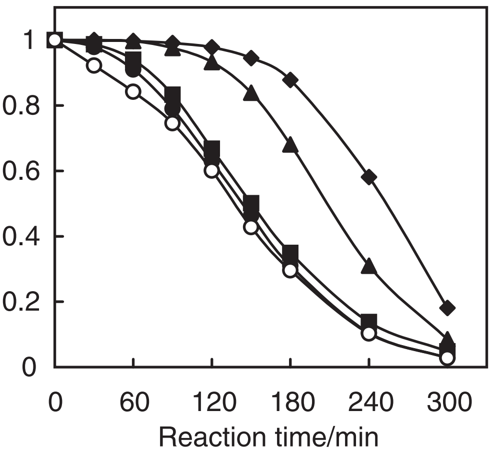
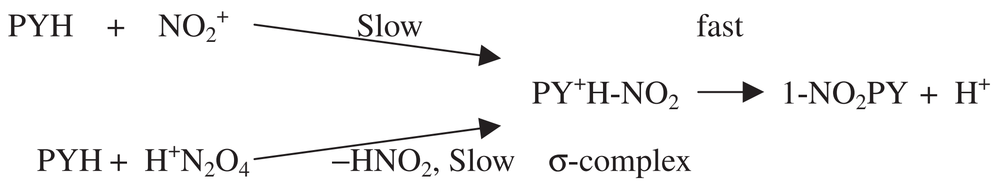


Fig. 14. Effect of previous aeration time of HNO_2 gas and addition of urea on the decay of PYH by NO_2. ●: 0 min, ■: 20 min, ▲: 80 min, ◆: 120 min, ○: [urea] = 2.48 $mmol\,dm^{-3}$, [PYH] = 1.24 $mmol\,dm^{-3}$, $[NO_2] = 100$ ppm, $[HNO_2] = 11.1$ ppm.



Scheme 1. Two possible nitration mechanisms.

concentration caused by the hydrolysis of N_2O_4 by trace water in polar solvents, a weakly electrophilic reagent, $H^+N_2O_4$, can be formed by the protonation of N_2O_4, which is responsible for the remarkably mild, efficient and selective nitration of PAH by N_2O_4. When an excess amount of H_2SO_4 ($[H_2SO_4]/a = 2$) was used, as shown in Fig. 5a, the decay curve of PYH fell between two curves of $c/a = 2.9$ and 4.5 in Fig. 10. This result shows that H_2SO_4, a stronger acid than HNO_3, is more potent than HNO_3 for intensifying the autocatalysis. In Eq. 7, an increased concentration of H^+ promotes the dissociation of $H^+N_2O_4$, and would accelerate the reaction of $NO_2{}^+$ with PYH. Considering the effects of HNO_2 and urea on the nitration of PYH (Fig. 14) and the promotion of the nitration after the accumulation of H^+, we consider that the nitration mechanism through $NO_2{}^+$ is more probable. Based on the substituent effect (Fig. 8), an electrophilic attack of $NO_2{}^+$ on PYH can be regarded as the rate-determining step.

The presence of an induction period for the nitration of PYH by NO_2 can be explained by the accumulation of N_2O_4 after the formation of HNO_3 (Eqs. 1–3) and the pre-equilibrium generating $NO_2{}^+$, that is, the protonation of N_2O_4 and the dissociation of $H^+N_2O_4$ (Eq. 7). Ingold et al.[25] studied an autocatalyzed nitration of halogen- and carboxyl-substituted benzenes by N_2O_5 in CCl_4, and concluded that $NO_2{}^+$ arising from the ionizing action of HNO_3 produced during the nitration is the nitrating species. They suggested the pre-equilibrium that $NO_2{}^+$ is progressively freed by the solvating HNO_3 from the influence of anions ($N_2O_5 + (x+y)HNO_3 \rightleftharpoons NO_2{}^+ (xHNO_3) + NO_3{}^-(yHNO_3)$).

It is known that the nitration mechanism of PAH with NO_2/N_2O_4 depends on the polarity[2,3,5,6,9] and dielectric constant[7] of solvents. In CCl_4, the exclusive pathway is a free-radical,[5–7] while in CH_2Cl_2, the ionic reaction pathway predominates[2,3,5,7,8] and is subject to efficient acid catalysis.[3,6,7] Pryor et al.[2] suggested that the more easily ionized PAH undergo nitration of the ET mechanism by NO_2/N_2O_4 in CH_2Cl_2. The ET mechanism was also suggested for the reaction of PAH[11] and alkylbenzenes[8,9] with NO_2/N_2O_4 in CH_2Cl_2. Eberson and Ladner[3,4] pointed out that the mechanism of NO_2/N_2O_4 nitration is fairly complex, and more work is needed to establish its mechanism with any degree of certainty. Compared with the nitration mechanisms described above, the H^+ autocatalyzed nitration mechanism proposed by us is the first found for the nitration of PAH using NO_2 as a nitrating reagent.

Comparison with the Nitration on Silica Particles. We have previously reported that heterogeneous nitration of PYH with NO_2 is reasonably explained by the facts that dissociated H^+ of HNO_3, accumulated by the reaction of NO_2 with the adsorbed water on silica particles, acts as an autocatalyst and a resultant $HNO_2{}^+/HN_2O_4{}^+$ attack at a carbon atom having a high electron density.[16] The decrease in PYH proceeded along sigmoid curves, however, we could not kinetically explain the nitration process. In the nitration of PYH in acetonitrile, the effects of the NO_2 and the added HNO_3 concentrations were similar to those on silica gel, however, both nitration mechanisms appear to be different because the nitration on silica gel was accelerated by coexisting HNO_2 gas (6 ppm/N_2) in NO_2 (6 ppm/N_2). In the presence of HNO_2 gas, we suggested another mechanism, that H^+ dissociated from accumulated HNO_3 transformed HNO_2 into NO^+ ($HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O$) and the NO^+ attacks NO_2/N_2O_4 to form $NONO_2{}^+/NON_2O_4{}^+$ as electrophiles.[17,18] The results of the proton autocatalytic nitration of PYH in solutions suggest that the atmospheric nitration of PAH by NO_2 would be promoted on the SPM adsorbed atmospheric HNO_3 and H_2SO_4 mists.

In conclusion, we were able to explain the kinetics of the H^+ autocatalytic nitration of PYH by aerating NO_2, and suggested an ionic electrophilic substitution mechanism involving $NO_2{}^+$ as an electrophile. The autocatalytic nitration is the first example found for the nitration of PAH carried out in organic solutions containing NO_2/N_2O_4 with or without acids.

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