

Basic research on the formation characteristics of nitrated polycyclic aromatic hydrocarbons in the combustion process

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Abstract

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) are widespread environmental pollutants that are generated by incomplete combustion. Many nitro-PAHs compounds are potential genotoxins and some are direct acting mutagens. Laboratory experiments using PAHs(pyrene, anthracene and naphthalene) in gas with coexisting nitrogen oxide and oxygen were conducted to elucidate the formation and decomposition behaviors of nitro-PAHs in the heating-reaction tube. It was found that the nitro-PAHs formed in a wide range of temperature from around 200–1000°C, and that the concentrations of most the nitro-PAHs decreased with increasing heating temperature (700–1000 °C).

Keywords: heating-reaction tube, polycyclic aromatic hydrocarbon, nitration, formation characteristic, temperature dependence.

1 Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) have been a focus of considerable concerns as potential mutagens and carcinogens [1]. Once released into the atmosphere, nitro-PAHs are highly persistent in the environment and can be transported long distances from their original sources [2,3]. Nitro-PAHs in the environment originate mainly from direct emissions from combustion sources, especially from diesel exhaust¹. Nitro-PAHs emissions from municipal solid waste (MSW) incinerators have been studied using bioassays [4–7]. The results of quantitative analysis of nitro-PAHs in emissions of MSW incinerators have also been reported [8,9]. In these studies, however, a limited number of



nitro-PAHs were studied only in final exit gases and ashes, and there is no information on the formation and decomposition behaviors of various nitro-PAHs in waste combustion. We conducted laboratory experiments using PAHs(pyrene, anthracene and naphthalene) in gas with coexisting nitrogen oxide and oxygen to elucidate the formation and decomposition behaviors of nitro-PAHs in a heating-reaction tube (hereinafter referred to as “reaction tube”).

2 Experimental procedures

2.1 Experimental apparatus and conditions

Laboratory experiments were conducted in a horizontal cell type electric muffle furnace equipped with a quartz tube, 27mm in diameter, and 800mm in length. The furnace was connected to a permeator set to high temperature, as shown in Figure 1.

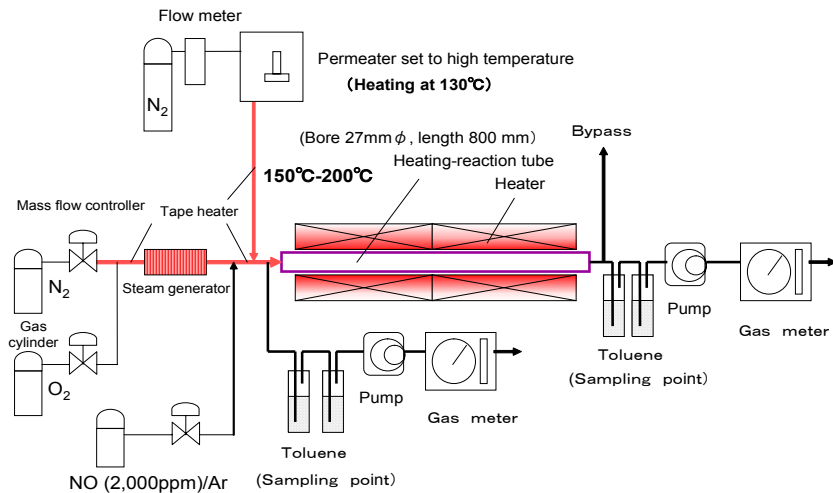


Figure 1: Schematic of experimental apparatus showing heating reaction flow.

Laboratory experiments were conducted using representative PAHs (pyrene, anthracene and naphthalene) in gas with coexisting nitrogen oxide (nitric oxide: NO) and oxygen (O_2). The heating temperature of the furnace was raised in the range of 200 – $1000^\circ C$. Similarly to waste incinerators, the concentrations of O_2 and NO were 10% and 150ppm, respectively. Little reaction activity of nitrous oxide (N_2O) was seen, but NO_x were generated at heating temperature of $900^\circ C$ and $1000^\circ C$, as shown in Figure 2. Experiments using N_2O were therefore conducted under two conditions at $900^\circ C$ and $1000^\circ C$.

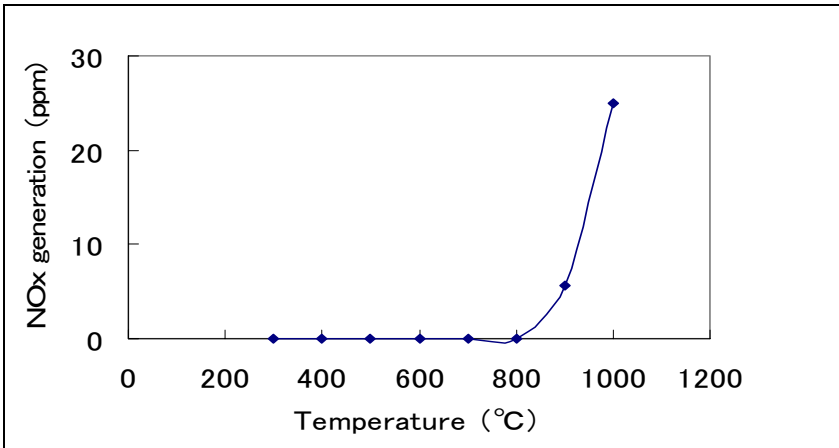


Figure 2: Correlation of N_2O supply and NO_x generation at outlet of reaction tube.

2.2 Sampling and analysis

Using the sampling system shown in Figure 1, gas was basically collected with toluene at the inlet and outlet of the heating-reaction tube. The typical sampling volume was 120-360L. During sampling the temperature of the sampling duct was maintained at 150-200°C by a tape heater. Identification and quantification of PAHs and nitro-PAHs were performed using gas chromatography-mass spectrometry with selected ion monitoring (GC/MS-SIM). An example of a chromatogram obtained by GC/MS-SIM is shown in Figure 3.

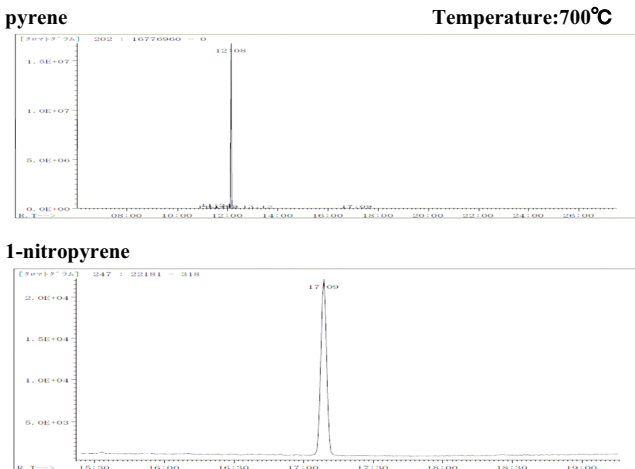


Figure 3: Example of chromatogram obtained by GC/MS-SIM at outlet of reaction tube.

3 Results and discussion

3.1 Pyrene

The concentration of pyrene was about $60\mu\text{g}/\text{m}^3$ at the inlet of the reaction tube. Sampling and analysis were carried out twice and the mean value was obtained.

3.1.1 Temperature dependence of pyrene concentration at outlet of reaction tube

Figure 4 shows the concentration of pyrene at various reaction-tube temperature. As can be seen in the figure, the decomposition of pyrene was promoted in proportion to the heating temperature at temperatures exceeding 600°C , and the reduction was almost 100% at 900 and 1000°C . In the case of N_2O , the result was the same for NO.

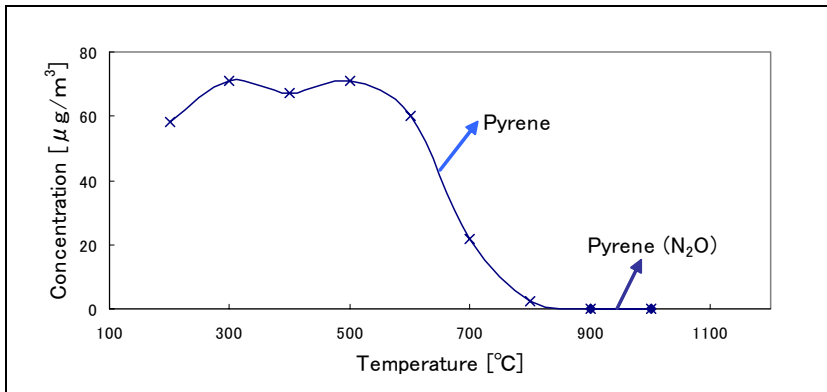


Figure 4: Temperature dependence of pyrene at the outlet of reaction tube.

3.1.2 Temperature dependence of nitropyrene concentration at outlet of reaction tube

Figure 5 shows the temperature dependence of 1-nitropyrene concentrations at the outlet of the reaction tube. In the heating experiment using pyrene, the base product of nitro-PAHs was 1-nitropyrene. As shown in the figure, the concentration of 1-nitropyrene was the highest ($6.2\mu\text{g}/\text{m}^3$) at a temperature of 300°C , then decreased with increasing temperature. Similarly to pyrene, the reduction was almost 100% at 900 and 1000°C .

3.1.3 Temperature dependence of dinitropyrene concentration at outlet of reaction tube

Figure 6 shows the concentration of dinitropyrene at various reaction-tube temperature. The products of dinitropyrene were 1,3- and 1,8-dinitropyrene. The concentrations of both products were highest at a temperature of 500°C , then decreased with increasing heating temperature. In the case of N_2O , however, the concentration of 1,8-dinitropyrene was slightly higher at 1000°C than that at 900°C .

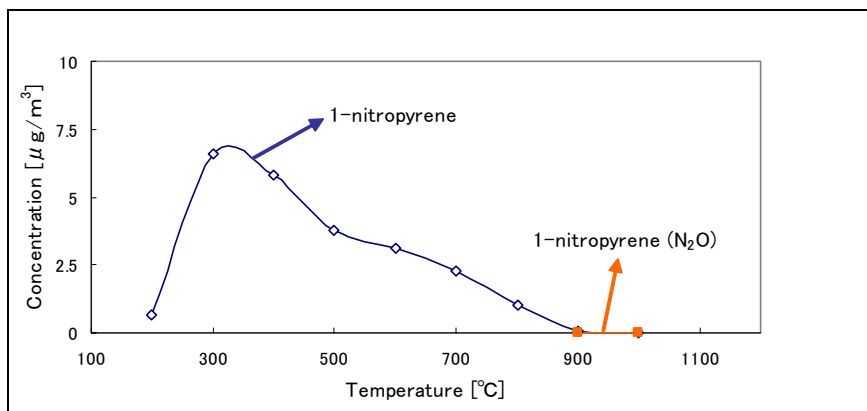


Figure 5: Temperature dependence of 1-nitropyrene at outlet of reaction tube.

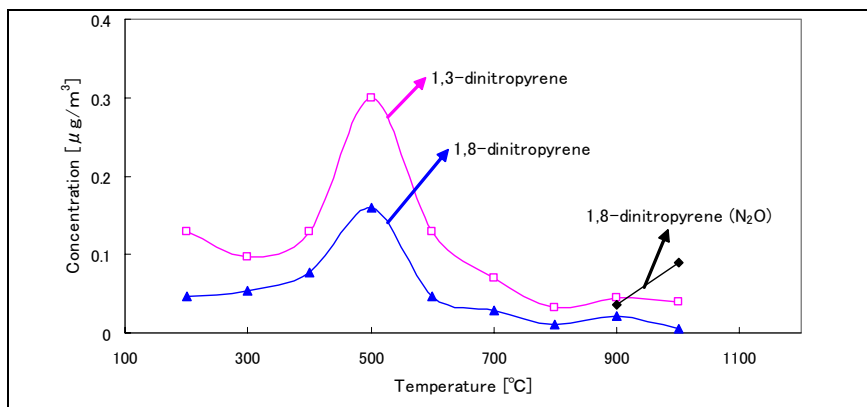


Figure 6: Temperature dependence of dinitro-PAHs at outlet of reaction tube.

3.2 Anthracene

The concentration of anthracene was about $100\mu\text{g}/\text{m}^3$ at the inlet of the reaction tube. Sampling and analysis were carried out twice and the mean value was obtained.

3.2.1 Temperature dependence of anthracene concentration at outlet of reaction tube

Figure 7 shows the concentration of anthracene at various reaction-tube temperature. It can be seen that the tendency of anthracene decomposition was similar to that of pyrene. The reduction was almost 100% at 900 and 1000°C.

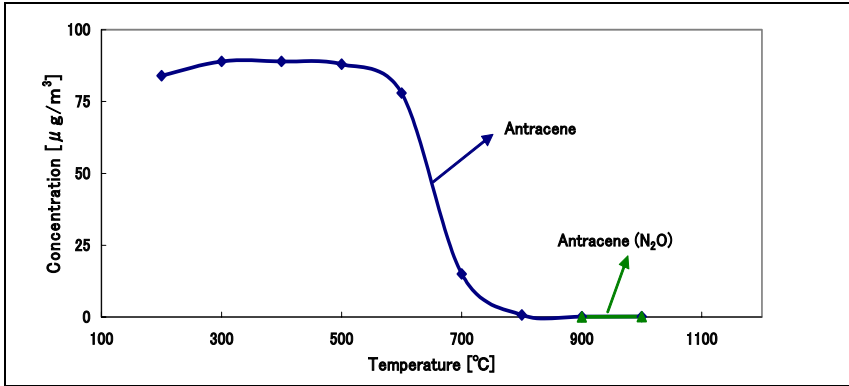


Figure 7: Temperature dependence of antracene at outlet of reaction tube.

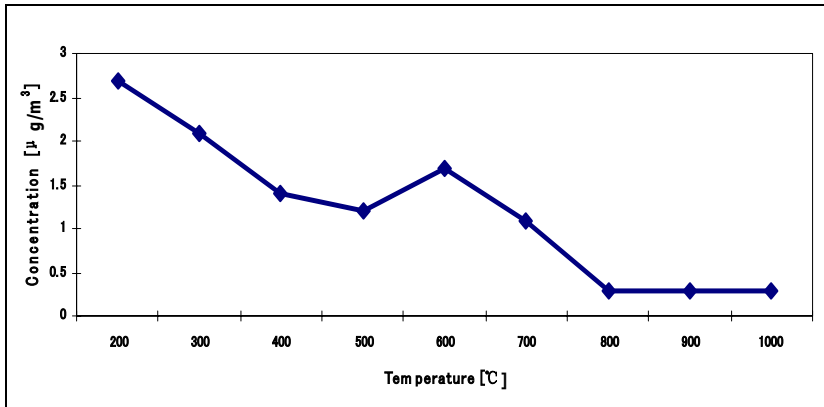


Figure 8: Temperature dependence of 9-nitroanthracene concentration at outlet of reaction tube.

3.2.2 Temperature dependence of nitroanthracene concentration at outlet of reaction tube

Figure 8 shows the temperature dependence of 9-nitroanthracene concentration at the outlet of the reaction tube. In the heating experiment using anthracene, the only nitro-PAHs product was 9-nitroanthracene.

As shown in the figure, the concentration of 9-nitroanthracene gradually decreased with increasing heating temperature.

3.3 Naphthalene

Using the sampling system of naphthalene shown in Figure 9, gas was basically collected with a Supelpak 20E tube matrix (polyurethane) (Supelco, Tokyo) at

the inlet and outlet of the reaction tube. The typical sampling volume was 120L. During sampling the temperature of the sampling duct was maintained at 50°C by a tape heater. Acetone was used for the extraction of naphthalene and nitronaphthalene.

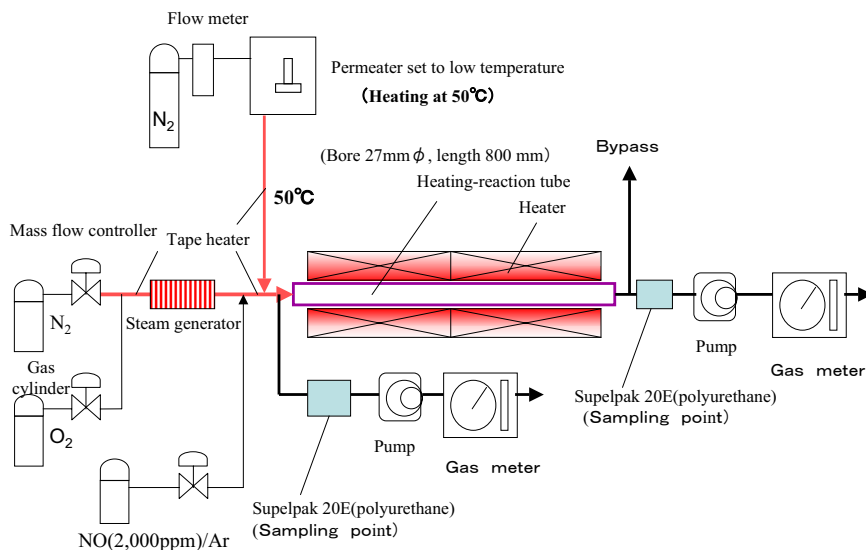


Figure 9: Schematic of experimental apparatus showing heating-reaction flow using naphthalene.

The concentration of naphthalene was about $100\mu\text{g}/\text{m}^3$ at the inlet of the reaction tube. Sampling and analysis were carried out twice and the mean value was obtained.

3.3.1 Temperature dependence of naphthalene concentration at outlet of reaction tube

Figure 10 shows the concentration of naphthalene at various reaction-tube temperature. It can be seen that the tendency of naphthalene decomposition was similar to that of anthracene. The reduction was almost 100% at 900 and 1000°C.

3.3.2 Temperature dependence of nitronaphthalene concentration at the outlet of heating-tube

In the heating experiment using naphthalene, there is no peak of nitro-PAHs at the chromatogram obtained by GC/MS-SIM.

4 Conclusions

- The decomposition of representative PAHs (pyrene, anthracene and naphthalene) was promoted in proportion to the heating temperature at temperature exceeding 600°C, and the reduction was almost 100% at 800–1000°C.



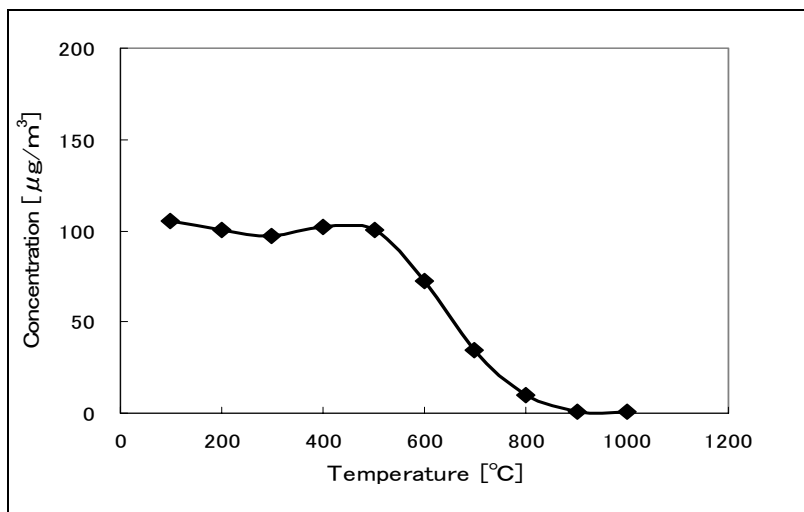


Figure 10: Temperature dependence of naphthalene at outlet of reaction tube.

- In the heating experiment using pyrene, the base product of nitro-PAHs was 1-nitropyrene. The concentration of 1-nitropyrene was highest ($6.2\mu\text{g}/\text{m}^3$) at a temperature 300°C , then decreased with increasing temperature. The reduction was almost 100% at temperature of 900°C or higher, similarly to pyrene.
- The products of dinitropyrene were 1,3- and 1,8-dinitropyrene. In the case of these dinitropyrene products, the concentrations were highest at a temperature of 500°C , then decreased with increasing temperature.
- In the heating experiment using anthracene, the only nitro-PAHs product was 9-nitroanthracene. The concentration of 9-nitroanthracene decreased with increasing temperature ($200\text{--}1000^\circ\text{C}$).
- In the heating experiment using naphthalene, the only nitro-PAHs product was 9-nitronaphthalene. The concentration of 1-nitronaphthalene decreased with increasing temperature ($100\text{--}1000^\circ\text{C}$).
- In the heating experiment using naphthalene, there is no peak of nitro-PAHs at the chromatogram obtained by GC/MS-SIM.

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