

FORMATION MECHANISM OF CHLORINATED PYRENE IN COMBUSTION OF POLYVINYL CHLORIDE

Miyake Y¹, Wang Q², Amagai T¹, and Horii Y³

¹ Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Suruga, Shizuoka, Japan;

² Graduate School of Integrated Pharmaceutical and Nutritional Sciences, University of Shizuoka, 52-1 Yada, Suruga, Shizuoka, Japan;

³ Center for Environmental Science in Saitama, 914 Kamitanadare, Kazo, Saitama, Japan;

Introduction

Polycyclic aromatic hydrocarbons (PAHs), which are suspected carcinogens and mutagens, are formed by incomplete combustion of organic compounds. Their chlorinated compounds (CIPAHs) such as chlorobenz[*a*]anthracene (ClBaA) and chlorobenzo[*a*]pyrene (ClBaP) are presumed to form in combustion of organic compounds containing chlorinated compounds and/or chloride. The CIPAHs have received worldwide attention because of their environmental persistence and widespread distribution^{1,2}. Horii *et al.* have showed that several CIPAHs and BrPAHs elicit dioxin-like activity with potencies comparable to those of several mono-ortho polychlorinated biphenyl (PCB) congeners³. Recent reports have showed the occurrence and profiles of CIPAHs and BrPAHs in flue gas and fly ash from municipal and industrial waste incinerators^{4,5}. However, little is known about formation mechanism of CIPAHs in combustion of chlorinated compounds.

This study was conducted to provide information on individual concentrations of 26 CIPAHs and their parent PAHs in combustion flue gas of polyvinyl chloride (PVC) at three different temperatures and residence times of gas in the furnace corresponding to reaction time. The formation mechanism of mono- to tetra-chlorinated pyrene, were dominant by-products in flue gas at all conditions were determined based on the analysis of reaction kinetics. The catalyzed formation of CIPAHs by metals was assumed not to occur in this study, due to the no inorganic compounds on combustion of PVC.

Materials and methods

Incineration. All the combustion experiments were performed in a horizontal and cylindrical furnace with a diameter of 28 mm and a length of 405 mm. The furnace has a stable temperature control (set temperature $\pm 5^\circ\text{C}$) and maximum temperature is 1000°C (QF-02; Dia Instruments Co., Ltd., Japan) (Figure 1). Combustion experiments were conducted with a powdered PVC at three different temperatures (800, 900, and 950°C), which are common combustion temperatures in municipal solid waste (MSW) incinerators. Mixture gas of pure oxygen (20%) and pure nitrogen (80%) was used in combustion. The residence times of gases in the furnace, corresponding to reaction time of CIPAHs, were set to be 2, 4, and 8 seconds by adjustment of gas flow at each temperature. A particular type of silica boat for sample introduction to the furnace was used to stabilize the burning rate of the sample, which is $10 \text{ kg}\cdot\text{h}^{-1}\cdot\text{m}^{-3}_{\text{N}}$. Duplicate combustion experiments were conducted at each operating condition.

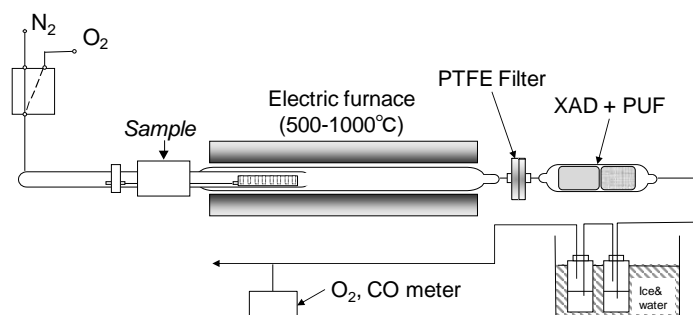


Figure 1. Experimental apparatus.

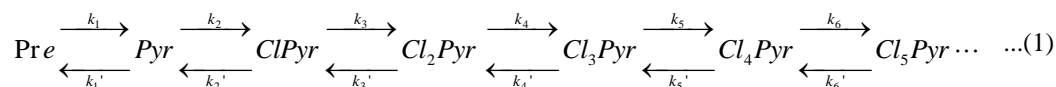
Samples and chemicals. Flue gas samples were collected from exits of the furnace in order to determine concentrations of CIPAHs. Sampling method of the samples was based on a modified standard method for PCDDs, PCDFs, and Co-PCBs⁶, which comprised of a Teflon-coated filter for collecting particle matter and a “PUF/XAD-2/PUF” cartridge (ORBO-1500, Supelco, USA) for collecting gas-phase CIPAHs. Twenty one individual CIPAHs (mono- to tetra-chloroPAHs) and their parent PAHs determined in this study were mono-chlorofluorene (ClFle), mono- to tri-chlorophenanthrene (Cl_nPhe: n=1-3), mono- to tetra-chloroanthracene (Cl_nAnt: n=1-4), mono- to di-chloro fluoranthene (Cl_nFlu: n=1-2), mono- to di-chloropyrene (Cl_nPyr: n=1-2), mono- to di-chlorochrysene (Cl_nChr: n=1-2), mono- to di-chloro benz[a]anthracene (Cl_nBaA: n= 1-2), and mono-chlorobenzo[a]pyrene. Isotope labeled ¹³C₆-phenanthrene, ¹³C₆-fluoranthene, ¹³C₆-chrysene, ¹³C₄-benzo[a]pyrene, ¹³C₆-chloropyrene, and ¹³C₆-chlorobenz[a]anthracene as internal standards and fluoranthene-d₁₀ as recovery standard were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

Analytical procedures. The determinations of CIPAHs were performed according to an established method with some modification^{4,5}. Briefly, samples were extracted using a soxhlet extraction method for the filter and cartridge, after spiking two nanograms each of internal standards. The solutions were purified, and fractionated using active carbon cartridge column (Carboxene 1016, 200 mg, Supelco, St. Louis, MO, USA) connected with silica gel cartridge column (Supelclean LC-Si, 2 g, Supelco) on the top. The cartridge columns were eluted with 20 mL of 10% dichloromethane/hexane. The silica gel cartridge was removed and the active carbon cartridge was reversed, then eluted with 120 mL of toluene. The toluene fraction that contained CIPAHs was concentrated and 2 ng of recovery standards were spiked.

Concentrations of CIPAHs were determined by gas chromatography-high resolution mass spectrometry (GC/HRMS; JMS-700V, JEOL, Tokyo, Japan). Gas chromatographic separation was accomplished by a 60-m BPX-DXN fused silica capillary column (0.25 mm i.d.; Kanto Chemical Co., Inc., Tokyo, Japan). Two microliters of the aliquot were injected in splitless mode at 280°C. The column oven temperature was programmed from 130°C (1 min) to 250°C at a rate of 5°C/min, and then to 320°C at 10°C/min; this was held for 18 min for CIPAH analysis. The MS was operated in an electron impact selected ion monitoring (SIM) at resolution R>10,000 (10% valley). Peaks were identified by comparison of the retention times of samples to standards if the signal-to-noise (S/N) ratio was >3, and were quantified if target/qualifier ion ratios were within 15% of the theoretical values. Any sample with recovery below 50% was discarded and reanalyzed.

Results and discussion

Potential chemical equation of chlorinated pyrene. Recent studies have shown that the direct chlorination of the parent PAHs can be the major mechanism of formation of CIPAHs in waste incinerators, due to a high correlation between Cl-/BrPAHs and its parent homologue emitted from waste incinerators⁴. The chlorination of pyrene would proceed consecutively with the participation of chlorine gas (Cl₂) and/or hydrogen chloride (HCl) gas. Thus, a potential chemical equation of chlorinated pyrene is as described below.



in which Pre is precursor of pyrene, Pyr is parent pyrene, Cl_nPyr is chlorinated pyrene (n=1-5), and *k* is rate constant of chemical reaction.

The chlorination of pyrene follows pseudo-first-order rate equation where the concentration of Cl₂ and HCl gas in furnace is present in large excess. The rate equation composes of a sum of formation and decomposition rate.

$$\frac{d[\text{Pre}]}{dt} = -k_1[\text{Pre}] + k_1'[\text{Pyr}]$$

$$\frac{d[\text{Pyr}]}{dt} = k_1[\text{Pre}] - k_2[\text{Pyr}] - k_1'[\text{Pyr}] + k_2'[\text{ClPyr}]$$

$$\frac{d[ClPyr]}{dt} = k_2[Pyr] - k_3[ClPyr] - k_2'[ClPyr] + k_3'[Cl_2Pyr]$$

$$\frac{d[Cl_nPyr]}{dt} = k_{n+1}[Cl_{n-1}Pyr] - k_{n+2}[Cl_nPyr] - k_{n+1}'[Cl_nPyr] + k_{n+2}'[Cl_{n+1}Pyr] \dots(2)$$

The difference method was generically used for solving the complex differential rate equations. Assuming small time $[t_n - t_{n-1}]$ is 0.01 second and initial concentration of precursor is 1000 nmol/m^3 , the rate constants are given by fitting curves to observed concentrations of parent pyrene and chlorinated pyrene.

$$\frac{[Pre]_{t_0} - [Pre]_{t_1}}{t_1 - t_0} = -k_1[Pre]_{t_1} - k_1'[Pyr]_{t_0}$$

$$\vdots$$

$$\frac{[Pre]_{t_n} - [Pre]_{t_{n-1}}}{t_n - t_{n-1}} = -k_1[Pre]_{t_n} - k_1'[Pyr]_{t_{n-1}}$$

$$\frac{[Cl_nPyr]_{t_n} - [Cl_nPyr]_{t_{n-1}}}{t_n - t_{n-1}} = k_{n+1}[Cl_{n-1}Pyr]_{t_n} - k_{n+2}[Cl_nPyr]_{t_{n-1}} - k_{n+1}'[Cl_nPyr]_{t_{n-1}} + k_{n+2}'[Cl_{n+1}Pyr]_{t_{n-1}} \dots(3)$$

Curve fitting to observed data set of chlorinated pyrene. The curve fitting results at combustion temperature of 800°C are shown in Figure 2. The concentrations of parent and chlorinated pyrene estimated from the proposed rate equations were well fitted with their observed concentrations from the combustion experiments of PVC at 800°C , 900°C , and 950°C . The rate constant of formation of mono- to tri-chlorinated pyrene (k_2, k_3, k_4) were over 30 times higher than those of tetra- to penta-chlorinated pyrene (k_5, k_6) ($k_4 > k_2 \approx k_3 \gg k_5 > k_6$). The formation rate constants k_n were higher than the decomposition rate constants k_n' at all combustion conditions. This suggested that the concentration of chlorinated pyrene consistently increase with increasing combustion temperature within the range of $800\text{-}950^\circ\text{C}$ and residence time within the range of 2-8 seconds.

The validity of the rate constant obtained by the curve fitting was confirmed by the empirical formula of Arrhenius, which gives the temperature dependence of the rate constant of a chemical reaction. The Arrhenius plots for formation rates of parent and chlorinated pyrene exhibited good linearity ($r^2 > 0.98$) (data not shown). These results indicated that the direct and sequential chlorination of the parent pyrene is the major mechanism of formation of chlorinated pyrene in gas phase (Figure 3).

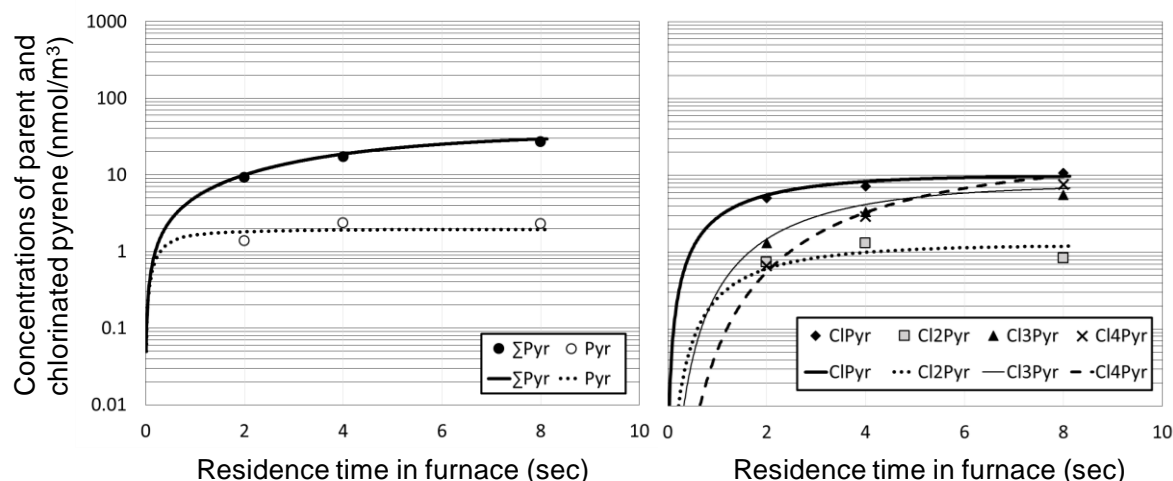


Figure 2. Curve fitting to observed concentrations of parent and chlorinated pyrene (800°C).

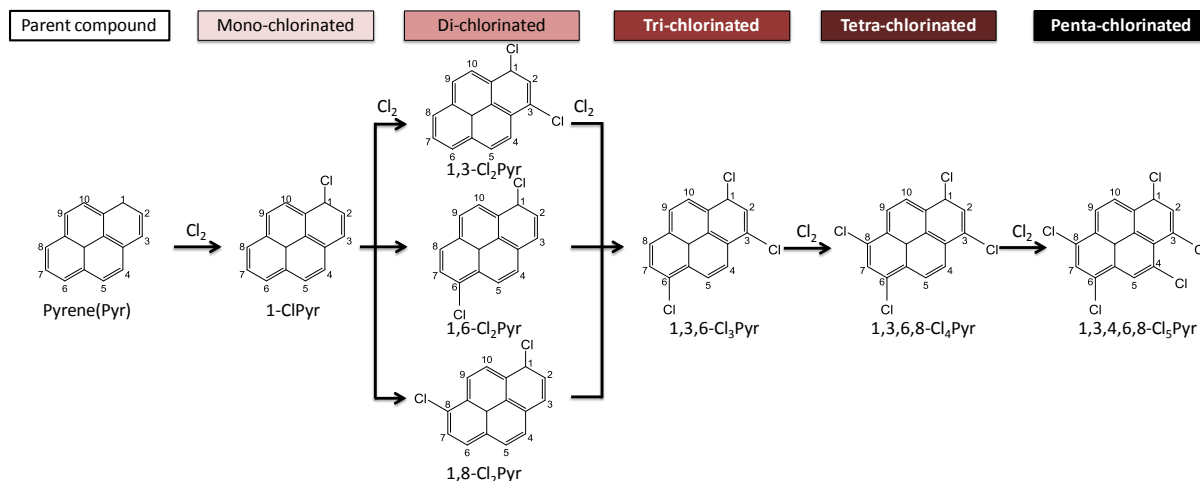


Figure 3. Formation pathway of chlorinated pyrene.

Highly-chlorinated pyrene. The proposed rate equation of chlorinated pyrene is possible to calculate the concentrations of penta-chlorinated pyrene, which have no analytical standards. The concentrations of penta-chlorinated pyrene were calculated to be comparable to those of tetra-chlorinated pyrene. From analysis of the molecular ion by HRGC/HRMS, the peaks of penta- and hexa-chlorinated pyrene were detected because the isotope patterns showed a high degree of similarity to theoretical isotope pattern of penta- and hexa-chlorinated pyrene. Further studies are needed to clarify the occurrence and behaviors of highly-chlorinated PAHs in the environment.

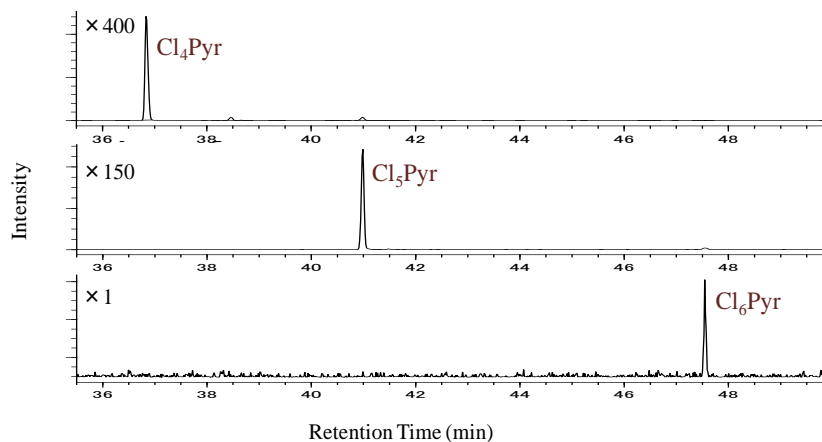


Figure 4. Chromatogram of highly-chlorinated pyrene.

Acknowledgements

Part of this study was supported by the Waste Management Research Grant, Ministry of the Environment, Japan (K113032) and Steel Foundation for Environmental Protection Technology.

References:

1. Horii Y, Ohura T, Yamashita N, Kannan K. (2009) *Arch Environ Contam Toxicol*. 57: 651-60.
2. Ohura T, Sawada K, Amagai T, Shinimiya M. (2009) *Environ Sci Technol*. 43: 2269-75.
3. Horii Y, Khim JS, Higley EB, Giesy JP, Ohura T, Kannan K. (2009) *Environ Sci Technol*. 43: 2159-65
4. Horii Y, Ok G, Ohura T, Kannan K. (2008) *Environ Sci Technol*. 42: 1904-9
5. Horii Y, Ohtsuka N, Minomo K, Nojiri K, Ohura T, Miyake Y, Kannan K. (2011); *Organohalogen Compd*. 73: 108-111
6. Japanese Standards Association. (2005) JIS K 0311:2005. Tokyo, Japan