

Suppression of PCDD/Fs formations by addition of hydrocarbons during combustion of chlorinated phenols

T. Kishi¹, S. Suzuki¹, T. Kawakami², K. Takeda¹ and S. Onodera¹

¹Faculty of Pharmaceutical Sciences, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan; ²Division of Medical Devices, National Institute of Health Sciences, 1-18-1 Kamiyoga, Setagaya-ku, Tokyo 158-8501, Japan.

Abstract

The thermal reactions of 2,4,6-T₃CP with hydrocarbons in a dry air stream was investigated using a silica flow reactor at residence time of 10 s and temperature range from 450 to 850 °C. The maximum molar yields of PCDD/Fs were observed at 650 °C on the combustion of each chlorinated phenol. Addition of hydrocarbons to chlorinated phenols showed remarkable decreasing in the yields of PCDD/Fs. The suppression effect on the formations of PCDD/Fs was dependent on the mixing ratio of hydrocarbons. Short-chain hydrocarbon showed relatively high suppression ratio. The pyrolytic products of hydrocarbons, such as alkyl radical and hydrogen radical would directly affect on the suppressing of PCDD/Fs formations during combustion of chlorinated phenols.

Introduction

Incineration process has been used as useful technique to reduce the volume of solid wastes from industrial and municipal activities. However, it is concerned about the emissions of hazardous by-products, especially polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), during incineration process. In the last three decades, the release of PCDD/Fs from combustion process has received much attention. In combustion process, two major pathways for the formation of PCDD/Fs had been identified: precursor mechanisms and *de novo* synthesis. Altwicker¹ suggested that the former route act an important role on the formation of PCDD/Fs. A number of studies about formation mechanism of PCDD/Fs had been performed, and these studies suggested that the chlorinated aromatic compounds, such as chlorinated benzenes and phenols, were greatly contributed to produce PCDD/Fs through heating²⁻⁵.

Chlorinated phenols have been often used for the combustion model experiments as PCDD/Fs precursors to elucidate the formation mechanism of PCDD/Fs in the combustion process^{6, 7}. However, precursors are not combusted as single chemical compound, but done with various kinds of co-existing materials in the actual incinerator. Thus, it is fully possible that the co-existing compounds influence in the PCDD/Fs formation reactions. Influence of co-existing materials which are present in the combustion chamber on the formation reactions of PCDD/Fs originated from precursors had also been examined. For example, sulfur or nitrogeous compounds were shown to reduce the concentration of PCDD/Fs in the exhaust gas⁸⁻¹¹. Therefore, it is important to study about influence of co-existent compounds on the formation reactions of PCDD/Fs.

In the previous studies, we had reported that remarkable decreasing of T₄CDDs was observed by addition of phthalate plasticizers during combustion of 2,4,6-T₃CP. Additionally, we suggested that the alkyl chain in the molecular structure of phthalate plasticizer might contribute to the suppression of T₄CDDs formations^{12, 13}. This

suppression effect is very important to clarify the formation mechanisms of PCDD/Fs in actual incinerators. However, it is still unknown whether these organic compounds have a suppression effect on the formation of PCDD/Fs through a precursor other than 2,4,6-T₃CP. Formation pathways of dibenzo-*p*-dioxin structure and dibenzofuran structure were considerably different, although they are both formed through the condensation of chlorinated phenols¹⁴. Therefore, it is necessary to examine the suppression effect on the formation of dibenzofuran structure, especially.

In this study, combustions of three kinds of chlorinated phenols (4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol) are studied using a laboratory-scale experimental apparatus in a dry air stream. Congener distributions of PCDD/Fs obtained from combustion of chlorinated phenols with or without hydrocarbon were analyzed. The aim of this work is to elucidate the suppression effect of hydrocarbons on the formation of PCDD/Fs.

Materials and Methods

Materials

Abbreviations of starting materials used in this study were summarized in Table 1. Combustion experiments were performed using chlorinated phenols and hydrocarbons obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan); their purities were over 98%, respectively. Dioxin compounds were not present in the starting materials as impurities before thermal treatment. All solvents used in this study were for pesticide residue and polychlorinated biphenyl analysis grade and were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The commercial standard substances of PCDD/Fs were obtained from AccuStandard Inc. (New Heaven, USA).

Table 1. Abbreviation of materials used in this study.

| PCDD/Fs precursors | |
|-------------------------|-----------------------|
| 4-MCP | 4-chlorophenol |
| 2,4-DCP | 2,4-dichlorophenol |
| 2,4,6-T ₃ CP | 2,4,6-trichlorophenol |
| hydrocarbons | |
| C15 | n-pentadecane |
| C20 | n-eicosane |
| C25 | n-pentacosane |
| C30 | n-triacontane |

Combustion

Fig. 1 illustrates a schematic diagram of the experimental apparatus. Experiments were performed using an electric furnace and a quartz reaction tube (400 mm in length and 20 mm in diameter). Five hundred microliter of starting material dissolved in diethyl ether (chlorinated phenols; 50 mmol l⁻¹, hydrocarbons; 0.5-5 mmol l⁻¹) was placed in a quartz sample boat and dried at room temperature. Then, starting material was thermally treated in a dry air stream by placing the quartz sample boat at the center of a preheated quartz reaction tube and heating it for 3 min. During the heating process, the airflow was regulated to maintain a constant residence time for approximately 10 s. The gaseous products formed during the thermal reaction were cooled and quenched in water and salted out with 15 g of NaCl; then, it was extracted twice with 40 ml of diethyl ether. After cooling to room temperature, the residual compounds in the reaction tube and quartz sample boat were rinsed with diethyl ether. After dehydrated with anhydrous sodium sulfate, the combined solvent was concentrated to approximately 1 ml by using a rotary evaporator and then to 0.1 ml under a gentle stream of dry nitrogen gas. Phenanthrene-d₁₀ was added to the concentrate as internal standard substances and the solvent was adjusted to 1 ml of toluene. Fifty microliter of analyte was derivatized with 50 μl of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) for GC/MS analysis.

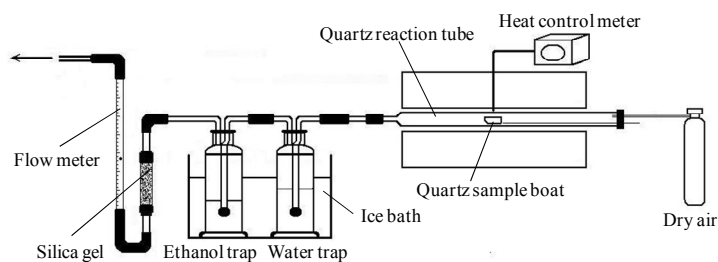


Fig. 1. Schematic diagram of experimental apparatus used for combustion of samples.

Analysis

Qualification of the combustion products was performed using a Varian CP-3800 gas chromatograph equipped with a fused silica capillary column (VF-5ms, 30 m × 0.25 mm i.d., 0.25 μm film thickness) coupled to a Saturn 2200 ion-trap mass spectrometer (Varian, Walnut Creek, CA, USA). The column oven temperature was programmed as follows: 40 °C for 3 min (initially), 40-220 °C at a rate of 20 °C min⁻¹, 220-300 °C at a rate of 8 °C min⁻¹ (held at 300 °C for 3 min). Helium was used as carrier gas at a constant flow-rate of 1 ml min⁻¹. The injector temperature was kept at 280°C, and 1 μl of each sample was injected in the splitless injection mode (0.75 min).

Quantification of the combustion products was carried out in the tandem mode (MS-MS). Table 2 lists the precursor ions selected in the MS-MS mode and the product ions selected for quantitative determination. For all the compounds, the maximum abundances of product ions were obtained using resonance excitation voltages, which were optimized by the automated method development (AMD) tool. Isolation mass windows of the precursor ions were set to ±3 *m/z*.

Calibration curves for the quantification of combustion products were determined by injecting solutions of commercial standard substances. In the case of PCDD/Fs, quantification was determined for a specific isomer and then applied to all the isomers having the same number of chlorine atoms.

Table 2. Optimized MS-MS parameters for the analysis of PCBzs, PCPs, PCDFs and PCDDs using the ion-trap mass analyzer Saturn 2200 MS

| Compounds | Precursor ions (m/z) | Waveform type | Excitation storage level (m/z) | CID (V) | Product ions (m/z) | Microscans | LOQ (ng ml ⁻¹) | LOD (ng ml ⁻¹) |
|------------------------------|----------------------|---------------|--------------------------------|---------|--------------------|------------|----------------------------|----------------------------|
| DCBz | 146 | Non-Resonant | 64.2 | 84 | 74 | 4 | 10 | 1 |
| T ₃ CBz | 182 | Non-Resonant | 75.0 | 88 | 109 | 4 | 10 | 2 |
| T ₄ CBz | 216 | Non-Resonant | 75.0 | 88 | 108 | 4 | 10 | 2 |
| P ₅ CBz | 250 | Non-Resonant | 80.0 | 86 | 142 | 4 | 50 | 10 |
| phenol-TMS | 151 | Non-Resonant | 66.4 | 76 | 93 | 4 | 10 | 1 |
| MCP-TMS | 185 | Non-Resonant | 81.4 | 74 | 149 | 4 | 10 | 2 |
| DCP-TMS | 219 | Non-Resonant | 96.5 | 74 | 183 | 4 | 10 | 2 |
| T ₃ CP-TMS | 255 | Non-Resonant | 112.4 | 92 | 217 | 4 | 10 | 2 |
| T ₄ CP-TMS | 289 | Non-Resonant | 110.0 | 80 | 251 | 4 | 20 | 5 |
| DF | 168 | Resonant | 73.9 | 0.9 | 139 | 4 | 10 | 2 |
| MCDF | 202 | Resonant | 89.0 | 0.8 | 139 | 4 | 10 | 5 |
| DCDF | 236 | Resonant | 104.0 | 1.6 | 173 | 4 | 10 | 5 |
| T ₃ CDF | 272 | Resonant | 119.9 | 2.1 | 209 | 4 | 10 | 5 |
| T ₄ CDF | 306 | Resonant | 135.0 | 1.2 | 243 | 4 | 10 | 5 |
| P ₅ CDF | 340 | Resonant | 150.0 | 1.4 | 277 | 4 | 25 | 10 |
| DD | 184 | Resonant | 81.0 | 0.8 | 128 | 4 | 10 | 2 |
| MCDD | 218 | Resonant | 96.0 | 0.9 | 155 | 4 | 10 | 5 |
| DCDD | 252 | Resonant | 111.1 | 0.6 | 189 | 4 | 10 | 5 |
| T ₃ CDD | 288 | Resonant | 127.0 | 1.1 | 225 | 4 | 10 | 5 |
| T ₄ CDD | 322 | Resonant | 142.0 | 1.6 | 249 | 4 | 10 | 5 |
| P ₅ CDD | 356 | Resonant | 157.1 | 1.6 | 293 | 4 | 25 | 10 |
| phenanthrene-d ₁₀ | 188 | Non-Resonant | 75.0 | 88 | 160 | 4 | - | - |

CID: Collision-induced dissociation, LOQ: Limit of quantification, LOD: Limit of detection, TMS: Trimethylsilyl

Results and Discussion

Isomer distribution of PCDD/Fs in the combustion of chlorinated phenols

At first, each of the chlorinated phenol was combusted alone to clarify the isomer distribution of PCDD/Fs in the absence of hydrocarbons. The major and minor products of PCDD/Fs were summarized in Table 3. The PCDD/Fs isomer patterns of the combustion products were similar to the previous studies¹⁵⁻¹⁷. On the combustion of each starting materials, PCDD/Fs were observed in the combustion samples at 500-800 °C. The maximum yields of total PCDD/Fs were obtained at 650 °C. The total yields of PCDD/Fs at 650 °C on the combustion of 2,4,6-T₃CP, 2,4-DCP and 4-MCP were 30.1, 5.33 and 26.4 mmol mol⁻¹, respectively.

Table 3. Observed PCDD/Fs products on the combustion of chlorinated phenols.

| starting materials | major products | minor products |
|-------------------------|---|---|
| 2,4,6-T ₃ CP | 1,3,6,8-/1,3,7,9-T ₄ CDD | T ₃ CDF 1,3,6,8-/2,4,6,8-T ₄ CDF two isomers of P ₅ CDF T ₃ CDD three isomers of P ₅ CDD |
| 2,4-DCP | 2,4,6,8-T ₄ CDF 2,7-/2,8-DCDD | 2,4,8-T ₃ CDF T ₃ CDD |
| 4-MCP | 2,8-DCDF | 2-MCDF |

Suppression of PCDD/Fs formations by hydrocarbons during combustion of chlorinated phenols

Mixture of each chlorinated phenol and C25 (the mixing ratio of C25 were 1% or 10% in molar ratio) was combusted at 450-850 °C. Fig. 2 shows the total yields of PCDD/Fs on the combustion of each starting material.

In Fig. 2-a, the total yields of PCDD/Fs on the combustion of 2,4,6-T₃CP decreased with increasing of mixing ratio of C25. We had already reported that yields of T₄CDDs decreased by mixing of phthalate esters during combustion of 2,4,6-T₃CP^{12, 13}. Similar tendency was also observed by mixing of C25. Additionally, the congener distributions of chlorinated aromatic compounds on the combustion products of 2,4,6-T₃CP with C25 were almost the same as that of combustion products of 2,4,6-T₃CP with phthalate esters (data not shown). These results suggested that the suppression mechanism of C25 in the formations of PCDD/Fs was the same as that of phthalate esters. The relative proportions of 1,3,6,8-/1,3,7,9-T₄CDDs was not changed by mixing of C25 as compared with combustion of 2,4,6-T₃CP alone. Therefore, C25 would not influence on the smiles rearrangement in the PCDD formation pathways.

Decreasing of PCDD/Fs by mixing of C25 was also observed on the combustion of 4-MCP and 2,4-DCP (Fig. 2-b and c). 4-MCP mainly formed DF structures on the combustion process, and PCDFs also decreased by mixing of C25. In the previous study, suppression of DD structures formations had already been demonstrated by combustion experiments of 2,4,6-T₃CP. On the basis of the present study, it was revealed that hydrocarbons suppressed formations of DF structures on the combustion of chlorinated phenols. This result might be suggested that the suppressing mechanisms of PCDD/Fs formations were to prevent phenoxy phenol formations, which is common process in the formation pathways of DD and DF structures. When hydrocarbon was combusted, alkyl radical and hydrogen radical were generated through decomposition of alkyl chain. These radicals might act as hydrogen donor to chlorinated phenols and prevent them from decomposition and condensation. Actually, the residual ratios of starting materials were slightly increased on the combustion of C25 mixture as compared with that of chlorinated phenols alone (data not shown). This result would confirm our prospective mechanism.

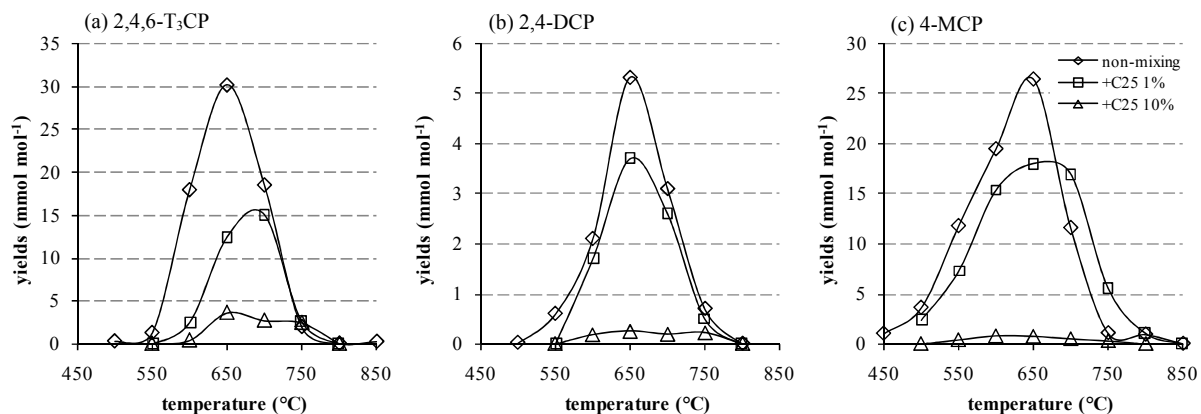


Fig. 2. Total yields of PCDD/Fs during combustion of 2,4,6-T₃CP (a), 2,4-DCP (b) and 4-MCP (c) with or without C25, as a function of temperature.

Influence of chain length of hydrocarbons on suppression of PCDD/Fs formations

Using various lengths of hydrocarbons (C15, 20, 25 and 30) as co-existing organic compounds, influence of chain length of hydrocarbons on the suppression of PCDD/Fs formations was examined. 2,4,6-T₃CP was used as PCDD/Fs precursor. Combustion experiments were accomplished by two mixing methods; the mixing amount was made constant by molar ratio or by weight (Fig. 3).

When combusted the mixture of 2,4,6-T₃CP and hydrocarbon (mixed by 100:1 in molar ratio), there was not a significant difference in the suppression ratio of PCDD/Fs between 4 kinds of hydrocarbons used in this study. Between C15 and C25, suppression ratio of PCDD/Fs was slightly high when longer hydrocarbon was mixed (Fig. 3-a). This result suggested that the suppression ratio might depend on the amount of carbon atom or hydrogen atom that exists in the furnace. However, suppression ratio of C30 was lower than that of C25. It might be due to the decomposition rate of each hydrocarbon. On the other hand, short-chain hydrocarbon showed high suppression ratio when mixing amount of hydrocarbons was made constant by weight (Fig. 3-b). Short-chain hydrocarbons were easier to decompose by heating and much more hydrogen radicals or alkyl radicals were generated than long-chain hydrocarbons¹⁸. Therefore, the pyrolytic products of hydrocarbons, such as hydrogen or low-molecular hydrocarbons would affect on the formation reactions of PCDD/Fs directly.

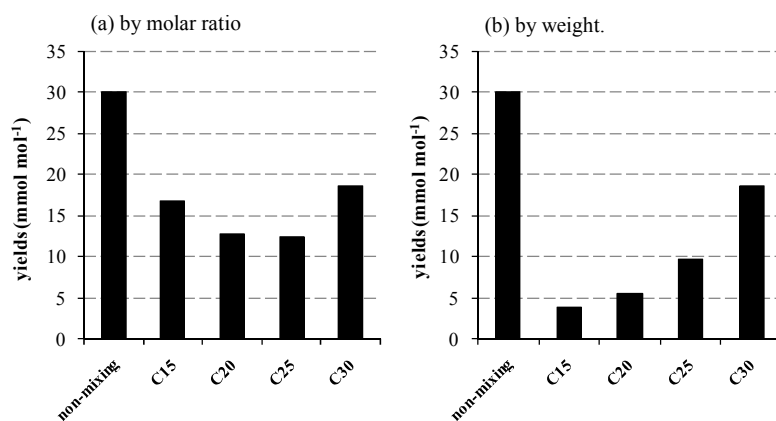


Fig. 3. Total yields of PCDD/Fs during combustion of 2,4,6-T₃CP with hydrocarbon at 650 °C. The mixing amount of hydrocarbon was made constant by molar ratio 1% (a) or by weight 125 µg (b)

Acknowledgements

The authors thank all the members of the Environmental Science Laboratory, Faculty of Pharmaceutical Sciences, Tokyo University of Science for their advice and support during this study. A part of this study was supported by Espec Foundation for Earth Environmental Research and Technologies.

References

1. Altwicker E.R. *Chemosphere* 1996; 33: 1897.
2. Altwicker E.R., Schonberg J.S., Konduri R. and Milligan M.S. *Hazard. Waste Hazard. Mater.* 1990; 7: 73.
3. Wikstrom E. and Marklund S. *Environ. Sci. Technol.* 2000; 43: 604.
4. Gullett B.K., Lemieux P.M., Lutes C.C., Winterrowd C.K. and Winters D.L. *Chemosphere* 2001; 43: 721.
5. Abad E., Martinez K., Caixach J. and Rivera J. *Chemosphere* 2006; 63: 570.
6. Evans, C.S. and Dellinger B. *Environ. Sci. Technol.* 2005; 39: 122.
7. Mulholland J.A. and Ryu, J.Y. *Combust. Sci. Technol.* 2001; 169: 107.
8. Raghunathan K. and Gullett B.K. *Environ. Sci. Technol.* 1996; 30: 1827.
9. Ruokojarvi P.H., Halonen I.A., Tuppurainen K.A., Tarhanen J. and Ruuskanen J. *Environ. Sci. Technol.* 1998; 32: 3099.
10. Ruokojarvi P.H., Asikainen A.H., Tuppurainen K.A. and Ruuskanen J. *Sci. Total Environ.* 2004; 325: 83.
11. Kuzuhara S., Sato H., Tsubouchi N., Ohtsuka Y. and Kasai E. *Environ. Sci. Technol.* 2005; 39: 795.
12. Shinkura T., Kishi T., Kawakami T. and Onodera S. *Organohalogen Compounds* 2007; 69: 1602.
13. Kishi T., Shinkura T., Suzuki S., Kawakami T. and Onodera S. *Organohalogen Compounds* 2008; 70: 2317.
14. Ryu J.Y., Choi K.C. and Mulholland J.A. *Chemosphere* 2006; 65: 1526.
15. Kim D.H., Mulholland J.A. and Ryu J.Y. *Proc. Combust. Inst.* 2005; 30: 1245.
16. Kim D.H., Mulholland J.A. and Ryu J.Y. *Chemosphere* 2007; 67: S135.
17. Kishi T., Suzuki S., Takagi M., Kawakami T. and Onodera S. *Chemosphere* 2009; 76: 205.
18. Watanabe M., Tsukagoshi M., Hirakoso H., Adschiri T. and Arai K. *AICHE J.* 2000; 46: 843.