Influences of metal oxides on the formation of PXDD/DFs during combustion of trihalogenated phenol gases

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Introduction

Environmental pollution by PXDD/DFs and related compounds has been the subject of public concern. These dioxins are mainly produced from municipal solid waste incinerators (MSWIs). In MSWIs, most of PXDD/DFs can be formed as by-products by the following two general pathways: (1) homogeneous, gas-phase reactions, and (2) heterogeneous, metal-mediated reactions[1-2]. It was reported that pathway (2) was considered to account for on the order of 70% of all dioxins formation[3]. Therefore, it has been studied well on the pathway (2) under low-temperature condition (200-500 °C) using metal compounds, which were in fly ash[4-6]. From these studies, it was cleared that copper and iron compounds promoted the PXDD/DFs formation[3,7-9]. On the other hand, inorganic compounds contained alkaline earth metal such as calcium and magnesium had suppressing effects on PCDD/DFs formation [6,10]. However, fly ash and bottom ash are also in a primary combustion furnace, and it is necessary to study the influences of metal oxides on the formation of PXDD/DFs under high-temperature condition (over 600 °C).

In this study, we reported analytical results on the major products of the pathway (1) of 2,4,6-trichlorophenol (2,4,6-T_3CP) or 2,4,6-tribromophenol (2,4,6-T_3BP) as precursors of PXDD/DFs. The amounts of starting materials, halogenated dioxins were studied as a function of temperature. The influences of metal oxides, copper oxide (CuO) or calcium oxide (CaO), on the PXDD/DFs formation from two trihalogenated phenols were also investigated under high-temperature ranging of 500-750°C in dry air stream.

Materials and Methods

Materials

Experiments were performed using 2,4,6-T_3CP, 2,4,6-T_3BP as precursors. These phenols were obtained from Tokyo Chemical Industry Co., Ltd. and their purities were >99 %. CuO, CaO as metal oxides were obtained from Kanto Chemical Co., Inc. and their purities were each >98% and >97%, respectively. Metal oxides were baked at 200 °C for 3 h to remove the impurities. No dioxin compounds as impurities were detected in the starting materials.

Thermal treatment

A laminar airflow, isothermal quartz reaction tube, 225 mm in length and 6 mm in diameter, was used to study the thermal formation of PXDD/DFs and its related compounds from each precursor (Fig. 1). In the quartz reaction tube, 50 mg of metal oxide was fixed at both ends with silica wool, adjusted about 10 mm of thickness, and was held at constant temperature. Each precursor dissolved in diethyl ether were placed on a platinum sample boat and dried at room temperature. Through the heating, the air flow rate and the temperature were regulated to keep constant. The evolved gaseous products were introduced to the water layer and ethanol layer in an ice bath and quenched. These gaseous products in the water layer were extracted twice by 30 ml of diethyl ether. After cooling to room temperature, the residue in the reaction tube, including metal oxide, was rinsed in diethyl ether and it was mixed with diethyl ether extract from the water layer. The combined solvent was concentrated to approximately 2 ml by a rotary evaporator and then concentrated to 1 ml under dry nitrogen gas stream. After addition of 2 ml of n-hexane was added to the sample, again concentrated to approximately 0.5 ml under dry nitrogen gas stream. Finally, phenanthrene-d_{10} dissolved in n-hexane as an internal standard substance (IS) was added and it was adjusted to 1 ml with n-hexane.
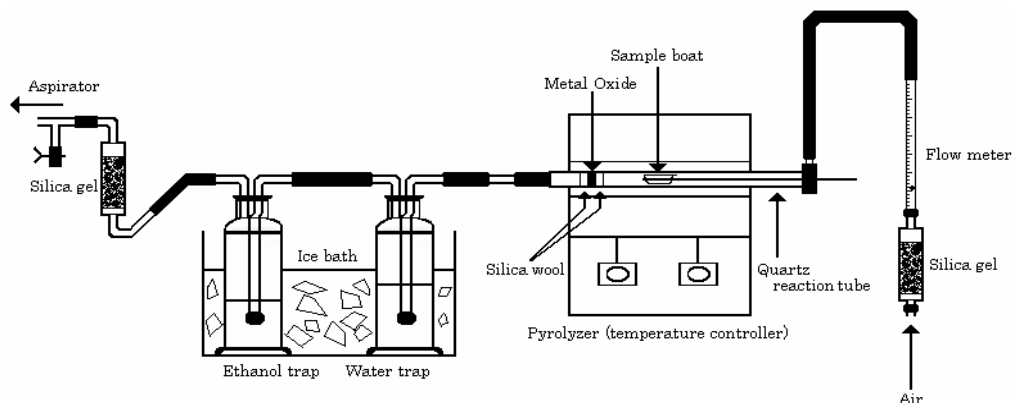
Fig. 1. Schematic diagram of experimental apparatus used for combustion of samples.

Analysis

PXDD/DFs and related compounds were quantified by using Shimadzu GC-14B gas-chromatograph equipped with flame ionization detector and with a fused silica capillary column (ZB-5, 30 m × 0.25 mm i.d., 0.25 μm film thickness). The column oven temperature was initially held at 60°C for 5 min. Secondly, it was raised to 220°C at 10°C/min, and then raised to 280°C at 4 °C /min. Finally, it was held at 280 °C for 10 min. On the other hand, these compounds were qualitified by using Varian CP-3800 gas chromatograph equipped with fused silica capillary column (VF-5ms, 30 m × 0.25 mm i.d., 0.25 μm film thickness) with Saturn 2200 mass spectrometer. In the first step, the column oven temperature was held at 60°C for 5 min. In the second step, it was raised to 220°C at 10 °C/min, and then raised to 280°C at 4 °C /min. Finally, it was held at 280 °C for 10 min. Products were identified with those of retention time and mass spectrum.

Results and Discussion

Compositions of products of trihalogenated phenols in a dry air stream

Numerous products were observed from the combustion of 2,4,6-trihalogenated phenols. Figures 2A and 2B show total ion chromatograms obtained from the combustion of 2,4,6-T$_3$CP and 2,4,6-T$_3$BP, respectively.
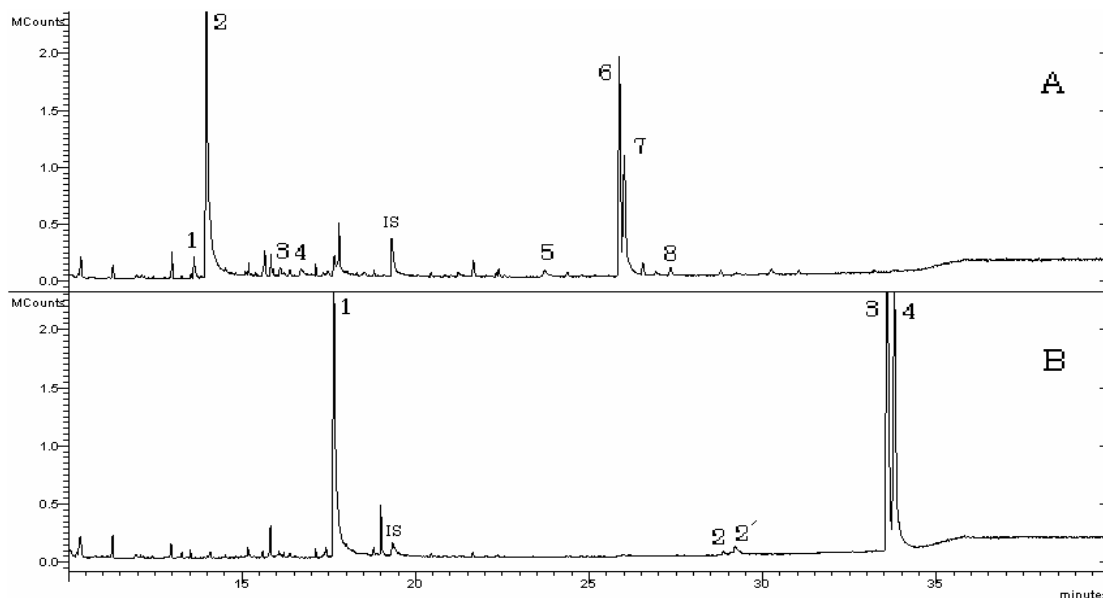

Fig 2. GC-MS total ion chromatograms of combustion products from 2,4,6-T$_3$XP.
A: 2,4,6-T$_3$CP at 700 °C, B: 2,4,6-T$_3$BP at 600 °C

In Figure 2A, starting material (peak 2) and two by-products (peaks 6 and 7) were mainly detected. The compounds, which were detected as peaks 6 and 7 were tetrachlorinated dibenzo-p-dioxins (T_4CDDs) as the most abundant intermediate products. Peak 6 was identified to be 1,3,6,8-T_4CDD, and peak 7 was identified to be 1,3,7,9-T_4CDD. Furthermore, four kinds of chlorophenol congeners (corresponding to the peak 4), three kinds of chlorobenzene congeners (corresponding to the peaks 1 and 3) were identified as the minor intermediates. At 700°C, trichlorinated dibenzo-p-dioxins (peak 5), tetrachlorinated dibenzofurans, pentachlorinated dibenzo-p-dioxins and hexachlorinated dibenzofurans (peak 8) were observed at trace level. At lower than 700°C, trichlorinated dibenzo-p-dioxins and pentachlorinated dibenzo-p-dioxins could not be observed.

As shown in Figure 2B, starting material (peak 1) and two by-products (peaks 3 and 4) were detected, latter compounds (peaks 3 and 4) were the most abundant intermediate products. Peak 3 and 4 were considered to be 1,3,6,8-tetrabrominated dibenzo-p-dioxin (1,3,6,8-T_4BDD) and 1,3,7,9-tetrabrominated dibenzo-p-dioxin (1,3,7,9-T_4BDD), respectively. Furthermore, two kinds of bromobenzene congeners, tetrabrominated dibenzofuran and pentabrominated dibenzo-p-dioxins were observed at trace level. Peaks 2 and 2' might be isomers of tribrominated dibenzo-p-dioxins.

Influence of temperature on the formation of PXDD/DFs.
The maximum amounts of two T_4CDDs (1,3,6,8-T_4CDD and 1,3,7,9-T_4CDD) obtained from the combustion of 2,4,6-T_3CP were about 2.2 % (mol/mol) of compounds at 700°C (Fig. 3). Similar phenomenon also occured about T_4BDD formation. The maximum amounts of two T_4BDDs (1,3,6,8-T_4BDD and 1,3,7,9-T_4BDD) obtained from the combustion of 2,4,6-T_3BP were about 3.3 % (mol/mol) of compounds at 600°C (Fig. 4). The temperature observed the maximum amounts of two T_4XDDs was somewhat higher than that of previous study[11]. This phenomenon was due to shortening the contacting time in the dry air stream.
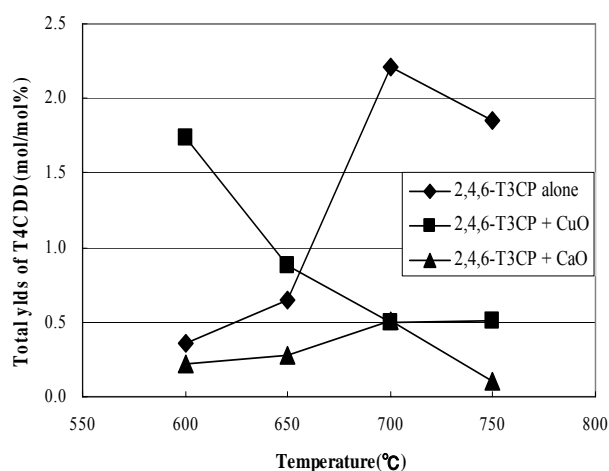

Fig 3. Influences of metal oxides on the total yields of T_4CDD from the combustion of 2,4,6-T_3CP, as a function of temperature (residence time: 2 sec).
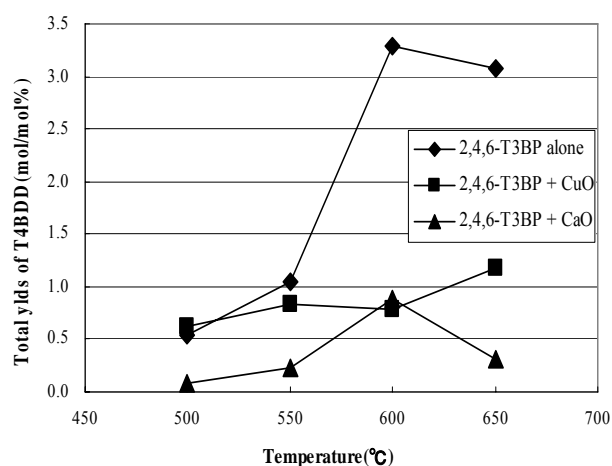
Fig 4. Influences of metal oxides on the total yields of T_4BDD from the combustion of 2,4,6-T_3BP, as a function of temperature (residence time: 2 sec).

Influence of contacting metal oxides on the formation of PXDD/DFs.
Under low-temperature condition (200-500 °C), copper compounds catalyzed the formation of PXDD/DFs during combustion of halogenated phenols, in contrast, calcium compounds suppressed the formation of PXDD/DFs. As shown in Fig. 3, CuO catalyzed the formation of T_4CDDs at 600°C and the total yields of T_4CDDs increased about 5 times, as compared with 2,4,6-T_3CP combustion without CuO. In the thermal reaction with CuO, most of 2,4,6-T_3CP might be decomposed. However, at 700°C, total amounts of T_4CDD decreased

about one fourth, as compared with 2,4,6-T_3CP combustion without CuO. Slightly catalytic effect on T_4BDDs formation by CuO was observed in the thermal reaction of 2,4,6-T_3BP at 500°C (Fig.4). On the other hand, suppressing effect on the total amount of T_4BDD was observed at 600°C, and it decreased about one sixth, as compared with 2,4,6-T_3BP combustion without CuO. This result might be influenced by the oxidative decomposition. The temperature observed decreasing of T_4CDDs and T_4BDDs amounts comparing with the combustion without CuO were over 660°C, and over 525°C, respectively.

Formation of T_4CDDs during the thermal reaction with CaO was suppressed at every temperature (Fig. 3). In this study, suppression ratios of T_4CDDs, as compared with T_4CDDs formation obtained for 2,4,6-T_3CP combustion without CaO, were 39.2-94.2 %. Formation of T_4BDDs during the thermal reaction with CaO was also suppressed at every temperature and suppression ratios of T_4BDDs, as compared with T_4BDDs formation obtained for 2,4,6-T_3BP combustion without CaO, were 72.9-89.7 %. In the previous studies, this preventing effect of T_4XDDs formations on 2,4,6-T_3XP combustion based on abstracting the proton of 2,4,6-T_3XP and giving electron were reported under low-temperature condition[6,10]. On the other hand, the amounts of T_4XDDs also decreased, as compared with 2,4,6-T_3CP combustion without CaO under high-temperature condition in our study, therefore, the same suppressing effect might be involving.

Conclusion
The thermal reactions of 2,4,6-T_3CP or 2,4,6-T_3BP in a dry air stream were studied using a laboratory-scale quartz tube reactor, with or without metal oxides. T_4XDDs as major products, and halogenated benzenes, phenols and other PXDD/DFs isomer as minor ones produced. Contacting with CuO, T_4CDDs formation from 2,4,6-T_3CP were promoted below about that temperature. However, decomposition effect of T_4CDDs by CuO was observed over 660°C. In contrast, T_4BDDs formation from 2,4,6-T_3BP were promoted below about 525°C, and were inverted over about that temperature. On the other hand, in the case of CaO, T_4XDDs formation were inhibited and yields of T_4XDD decreased at every temperature.

References
1. Stanmore B. R., *Combust. Flame* 2004; 136: 398.
2. Addink R., Olie K., *Environ. Sci. Technol.* 1995; 29: 1425.
3. Lomnicki S. and Dellinger B., *J. Phys. Chem. A*, 2003; 107: 4387.
4. Tupputanen K., Halonen I., Ruokojarvi P., Tarhanen J., Ruuskanen J., *Chemosphere* 1998; 36: 1493.
5. Kuzuhara S., Sato H., Kasai E., and Nakamura T., *Environ. Sci. Technol.* 2003; 37: 2431.
6. Yong Qian., Minghui Zheng., Wenbin Liu., Xiaodong Ma., and Bing Zhang., *Chemosphere* 2005; 60: 951.
7. Catherine S. Evans and Dellinger B., *Environ. Sci. Technol.* 2005; 39: 4857.
8. Onodera S., Nagano M. and Saitoh R., *Journal of Environmental Chemistry* 2007; 17: 17
9. Ryan SP., Altwicker ER., *Environ. Sci. Technol.* 2004; 38: 1408.
10. Liu WB., Zheng MH., Zhang B., Qian Y., Ma XD., Liu WX., *Chemosphere* 2005; 60: 785.
11. Sidhu S. S., Maqsud L. and Dellinger B., *Combust. Flame* 1995; 100: 11.