

Influence of experimental conditions on the PCDD/F formation in the thermal reactions of halogenated phenols

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Abstract

The thermal reactions of 2,4,6-trichlorophenol (2,4,6-TCP) or 2,4,6-tribromophenol (2,4,6-TBP) in an air stream were investigated using a 2 cm i.d., silica flow reactor at residence times of 0.2 ~10 s and temperatures from 250 to 800 °C. Pyrolysis of 2,4,6-TCP or 2,4,6-TBP in an air stream was shown to produce a variety of compounds, including two tetrahalogenated dibenzo-p-dioxins as the most abundant intermediate products, and halogenated benzenes, phenols, naphthalenes and dibenzofurans as trace species. The thermal reactions of 2,4,6-TCP or 2,4,6-TBP in an air stream at the different resident times or in the presence of organic matters were also examined, in order to examine their influences on the polyhalogenated dibenzo-p-dioxin and dibenzofuran formation.

Introduction

In municipal solid waste incinerators (MSWIs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) can be formed as byproducts by two general pathways: (A) homogeneous, gas-phase reactions, and (B) heterogeneous, metal-mediated reactions. The first route, which is observed in post-combustion gas at temperatures between 500 and 700 °C, occurs via precursors. The second route, which is observed in particle collection devices at temperatures between 250 and 450 °C, may involve precursors of similar structure (e.g. polychlorinated phenols, benzenes, and biphenyls) or particulate carbon (de novo synthesis). It has been reported that PCDD/Fs formation from (A) is 10^2 - 10^5 times faster than from (B) ¹⁻⁴.

Model studies showed that PCDD/Fs formation from precursors is likely predominance of the two proposed pathways (A) and (B) ⁵. Polychlorinated phenols are structurally closely related to PCDD/Fs and thought as important precursors for PCDD/Fs formation ⁶⁻⁷. Some mechanisms of PCDD/Fs formation from polychlorinated phenols as precursors have been reported ⁸⁻⁹. The importance of the gas-phase mechanism from precursors compared to both catalytic heterogeneous formation processes of dioxins remains controversial ¹⁰⁻¹³ due to the large uncertainties in the reaction pathways and the corresponding kinetics parameters proposed in the reaction kinetic model.

In this paper, we reported analytical results on the major stable products of the high-temperature, homogeneous gas-phase reactions of 2,4,6-trichlorophenol (2,4,6-TCP) or 2,4,6-tribromophenol (2,4,6-TBP). The concentration profiles of starting materials, halogenated dioxins and other pyrolysis product were determined as a function of temperature for various residence times. The influence of organic materials, such as diethylhexyl phthalate (DEHP), on the PCDD/Fs formation from 2,4,6-TCP or 2,4,6-TBP were also studied as a function of temperature.

Materials and Methods

Materials

Experiments were performed using 2,4,6-TCP, 2,4,6-TBP and DEHP. These samples were obtained from Tokyo chemical industry co. and their purities were over 99 %, respectively. No dioxin compounds as impurities were detected in the starting materials before thermal treatments.

Thermal treatment

A laminar flow, isothermal quartz reaction tube was used to study formations of dioxin related compounds from each material (Fig. 1). Each material dissolved in diethylether were placed on a quartz sample boat and dried at room temperature. Through the heating, the air flow was regulated to hold the residence time constant. The evolved gaseous products were introduced to the water and ethanol layers in an ice bath and quenched. After cooling to room temperature, the reaction tube was rinsed with diethylether and it was mixed with diethylether extract from the water layer. The combined solvent was concentrated to approximately 1 mL by a rotary

evaporator and then concentrated to 0.1 mL under dry nitrogen gas stream and adjusted to 1 mL with diethylether.

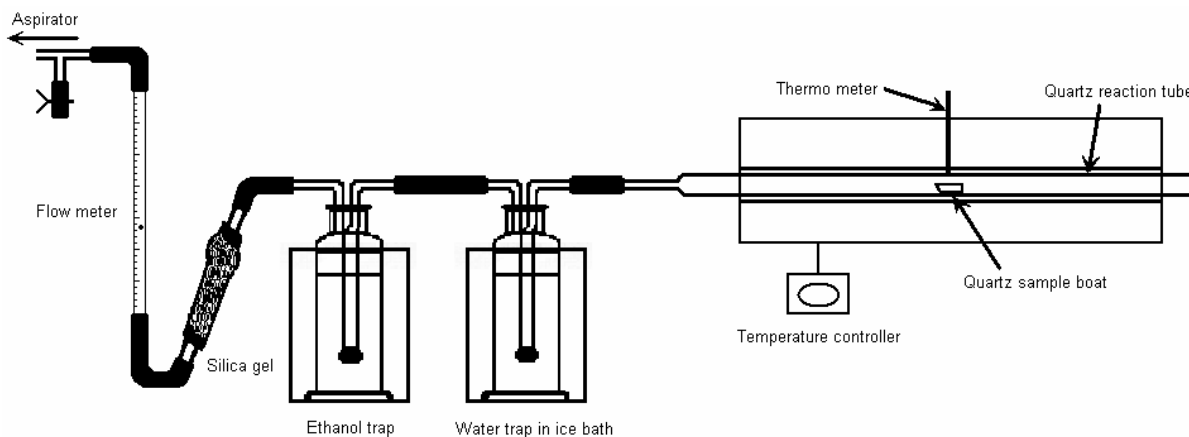


Fig. 1. Schematic diagram of experimental apparatus for pyrolysis of samples.

Analysis

Dioxin related compounds were quantified by Shimadzu GC-2010 gas-chromatograph equipped with flame ionization detector and with a fused silica capillary column (TC-5, 30 m \times 0.25 mm i.d., 0.25 μ m film thickness). The column oven temperature was initially held at 80 $^{\circ}$ C for 5 min. Then, it was raised to 280 $^{\circ}$ C at the rate of 10 $^{\circ}$ C/min. Finally, it was held at 280 $^{\circ}$ C for 10 min. On the other hand, these compounds were quantified by Varian CP-3800 gas chromatograph equipped with fused silica capillary column (VF-5ms, 30 m \times 0.25 mm i.d., 0.25 μ m film thickness) with Saturn 2200 mass spectrometer. The column oven temperature was initially held at 80 $^{\circ}$ C for 2 min. Then, it was raised to 280 $^{\circ}$ C at the rate of 10 $^{\circ}$ C/min. Finally, it was held at 280 $^{\circ}$ C for 10 min.

Results and Discussion

Thermal reactions of halogenated phenols in an air stream

2,4,6-TCP was fairly stable up to 300 $^{\circ}$ C for the residence time of 6 s, with slight decomposition starting at 350 $^{\circ}$ C. At 600 $^{\circ}$ C, 2,4,6-TCP in an air stream was shown to produce a variety of compounds, including two tetrachlorinated dibenzo-p-dioxins (1,3,6,8-TCDD and 1,3,7,9-TCDD) as the most abundant intermediate products (Fig. 2), and two chlorophenol congeners and three chlorobenzene congeners as the minor intermediates. Formation of tetrachlorinated dibenzofurans from 2,4,6-TCP was slightly observed in the gaseous samples. Over 700 $^{\circ}$ C, in addition to these products, small amount of chlorinated naphthalenes was detected in the evolved gaseous samples. On the other hand, 2,4,6-TBP was fairly stable up to 300 $^{\circ}$ C for the residence time of 6 s, with slight decomposition starting at 350 $^{\circ}$ C. At 600 $^{\circ}$ C, 2,4,6-TBP in an air stream was shown to produce a variety of compounds, including two tetrabrominated dibenzo-p-dioxins (may be 1,3,6,8-TBDD and 1,3,7,9-TBDD) as the most abundant intermediate products (Fig. 2), and two bromobenzenes as the trace species.

Influence of residence times on the dioxins formation

The most abundant intermediates (1,3,6,8-TCDD/1,3,7,9-TCDD) from gas-phase 2,4,6-TCP reaction were observed over temperature range 400 - 800 $^{\circ}$ C for residence time of 6 s (Fig. 2). Its maximum concentration occurred about 600 $^{\circ}$ C and corresponded to a molar percent yield of 3 %. In contrast with the 2,4,6-TCP reaction, the abundant products (may be 1,3,6,8-TBDD/1,3,7,9-TBDD) from gas-phase 2,4,6-TBP reaction were detected over temperature range 400 - 700 $^{\circ}$ C, with maximum concentration observable at 500 $^{\circ}$ C and with corresponding to a molar percent yield of 14 %. When 2,4,6-TCP was heated at 600 $^{\circ}$ C in an air stream, the molar percent yield of 0.5, 1.0 and 3.0 % were obtained for residence times of 2.0, 3.5 and 6.0 s, respectively (Fig. 3). But upon

heating over 800 °C, the molar percent yields decreased with an increase of the residence times. Similar phenomenon to the 2,4,6-TCP reaction was also observed for the dioxin formation in the gas-phase 2,4,6-TBP reactions.

Influence of Adding organic matters on the dioxin formation

Many inorganic and organic compounds have been studied for control of PCDD/Fs. These studies mostly focus on the deactivation of the catalysis mainly Cu compounds with inorganic or organic N- or S- compounds¹⁴⁾, and reduction of the acidic chlorine resources such as HCl and Cl₂ with basic compounds in MSWIs¹⁵⁾. But the inhibition mechanism with these substances in the dioxin formation was not well understand. Therefore, further experiments were performed to understand the influence of adding organic compounds on the dioxin formation from the gas-phase 2,4,6-TCP or 2,4,6-TBP reactions.

As can be seen in Fig. 3, addition of DEHP (5 mg) to 2,4,6-TCP (5 mg) was shown to reduce amount of TCDD formation at temperature range 400 to 700 °C for residence time of 6 s. Suppressing effects on the total amount of TCDD formation were observed after mixing of 0.5 mg DEHP into gas-phase 2,4,6-TCP at 600 °C for the same residence time. The suppressing effects increased with increasing in the amount of adding DEHP into gaseous 2,4,6-TCP. Similar suppressing effect was also observed for TBDD formation from the gas-phase 2,4,6-TBP reactions.

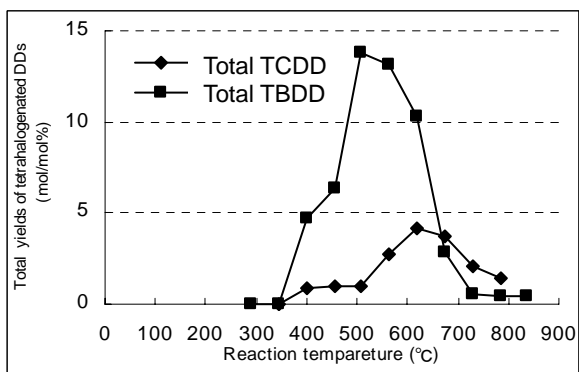


Fig. 2. Total yields of TCDD/TBDD formation from gas-phase 2,4,6-TCP/2,4,6-TBP reactions, as a function of reaction temperature for residence time of 6 s.

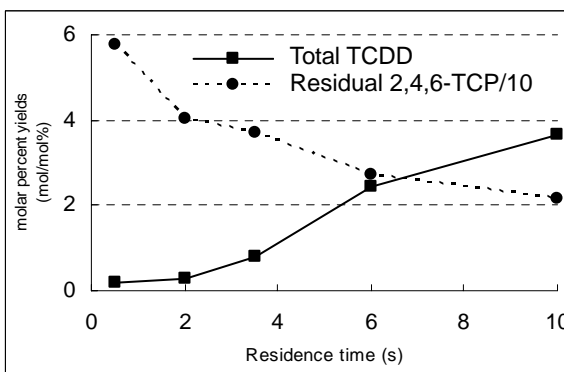


Fig. 3. Total yields of TCDD formation and residual ratio of 2,4,6-TCP from gas-phase 2,4,6-TCP reactions at 600 °C, as a function of residence time.

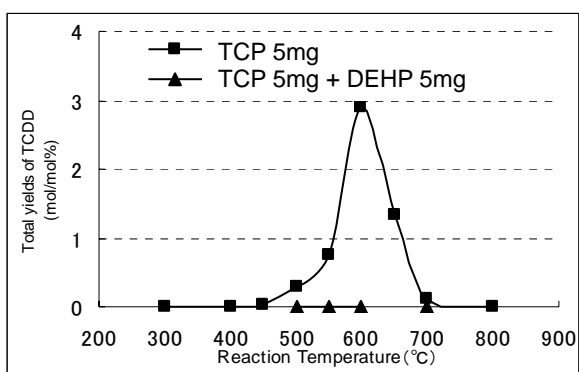


Fig. 4. TCDD formation from 2,4,6-TCP in the gas-phase reactions and suppressing effects of DEHP on the TCDD formation, as a function of temperature for residence time of 6 s.

Conclusion

The thermal reactions of 2,4,6-TCP or 2,4,6-TBP in air was investigated using a silica flow reactor at different residence times and temperatures from 350 to 800 °C. Gas-phase reactions of these compounds yielded TCDDs or TBDDs as major products and halogenated benzenes, naphthalens and other DDs and DFs as minor ones. The TCDD formation from 2,4,6-TCP was observed at temperature range 400 to 800 °C. The maximum molar percent yield of TCDDs was 4 % when TCP was heated at 600 °C. While, the TBDD formation from 2,4,6-TBP was detectable at temperature range 350 to 700 °C. The maximum molar percent yield of TBDDs was 14 % when TBP was heated at 500 °C. Suppressing effect on the TCDD and TBDD formation from the dioxin precursors was also observed at the temperature ranges examined when precursors were heated with DEHP.

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