Thermodynamic Behaviors of Polybrominated/chlorinated Dibenzo-p-dioxins in Flue Gas

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Introduction

The brominated dioxins apparently arise under thermal stress, because BFRs appear to be their main source in incinerators. However, the formation behaviours of brominated dioxin congeners from incinerators remain unclear. One of the reasons for our lack of understanding is that current analytical methods are able to detect, but not quantify, all of the mixed brominated/chlorinated congeners. Because of the complexity of analytical procedures and lack of reference standards, it has been possible to characterize and determine only a small number of polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) and polybrominated/chlorinated dibenzo-p-dioxins and furans (PXDD/Fs) isomers.

We recently reported the calculated heat capacities, standard enthalpies of formation and entropies for 75 PBDDs, 135 PBDFs and 339 PXDDs using the density functional theory (DFT).[1-3)] In the present study, we consider their formation and decomposition thermodynamically, by conducting equilibrium thermodynamic simulations of the flue gas of flame retardant combustion at various temperatures and at different bromine/chlorine ratios in the source.

Methods and Materials

DFT calculation: In earlier reports[1-3)], we have presented tables of consistent sets of thermodynamic data for the PBDD/Fs and PXDDs. The detailed computational methods used to obtain the thermodynamic data for the dioxins and furans also appear in these papers. In the calculations, we used Gaussian 98 software to implement the density functional theory (DFT) to calculate the heat capacities (C_P), absolute entropies (S) and enthalpies of formation (ΔH^o_f) at 298K. We were able to derive the standard free energies of formation (ΔG^o_f) from the values of C_P, S and ΔH^o_f. In earlier reports, tables of consistent sets of thermodynamic data for the PBDD/Fs and PXDDs were presented.[1-3)]

Thermodynamic simulation: To elucidate the effect of temperature and gas composition, we simulated the formation of PCDDs, PBDDs and PXDDs thermodynamically in the flue gas of the brominated flame retardant combuster. We used the FactSage software to recompile the thermodynamic data of 75 PCDDs [4,5)], 75 PBDDs [1,2)] and 339 PXDDs [3)] and for the equilibrium thermodynamic calculations. Other 78 gaseous species in the FactSage database were selected for the calculations.

Results and Discussion

Standard free energy of formation: Figure 1 shows the average standard free energy of formation (ΔG^{o}_{f}) for each PXDD homologue within the same degrees of bromination and chlorination at 298K. In Fig.3, we can see that as the degree of bromination of the PXDDs increases, their ΔG^{o}_{f} increase, but decreases slightly with an increase in the chlorination/bromination ratio. Other investigators have suggested that the relative thermodynamic stability is affected by the intramolecular repulsion effect.[6)] The large repulsion energy of Br-Br relative to that of Cl-Cl, due to the larger size of the bromine atom, tends to make the molecule unstable.

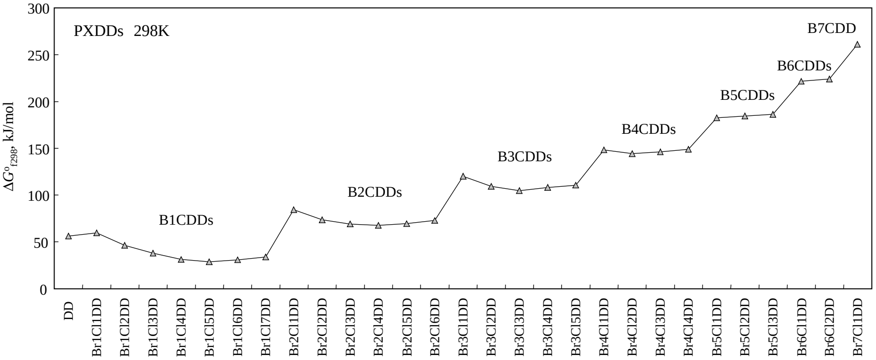

Fig.1: Average standard free energies of formation for each PXDD homologue within the same degrees of bromination and chlorination at 298K.

Potential diagram for TeXDDs: Figure 2 shows the bromine-chlorine equilibrium potentials for the formation of 2,3,7,8- TeXDDs ($BrmCl_{(4-m)}DD$) from 2,3,7,8-TeCDD at 573K, where these potentials are represented by the partial pressures of Br_2 and Cl_2. The diagram is based on the bromination reaction of 2,3,7,8-TeCDD as shown in the following equation:

$$2/m\ \mathrm{TeCDD} + \mathrm{Br_2(g)} = 2/m\ \mathrm{BrmCl_{(4\text{-}m)}DD} + \mathrm{Cl_2(g)},\quad (m=1,2,3,4) \tag{1}$$

$$\Delta G^{o}_{r} = -RT\ln K = -RT\ln\frac{P^{2/m}_{Br_mCl_{(4-m)}DD}P_{Cl_2}}{P^{2/m}_{TeCDD}P_{Br_2}} \tag{2}$$

where K and P indicate the equilibrium constant for the reaction and the partial pressure, respectively. In this diagram, we assumed that in order to determine easily the thermodynamic possibility of bromination of the chlorinated dioxin congeners. The diagram shows that each 2,3,7,8-TeXDD can be thermodynamically formed from 2,3,7,8-TeCDD at a higher bromine potential than that denoted by each solid line. The dotted lines give the equilibrium potentials of bromine and chlorine for the relationship between the gaseous HCl and HBr at their several partial pressure ratios based on the following reaction:

$$2HCl(g) + Br_2(g) = 2HBr(g) + Cl_2(g) \tag{3}$$

$$\Delta G^{o}{}_{r} = -RT \ln K = -RT \ln \frac{P_{HBr}^{1/2} P_{Cl_2}}{P_{HCl}^{1/2} P_{Br_2}} \tag{4}$$

Using this diagram, we can distinguish and discuss the likelihood that a particular 2,3,7,8-TeXDD is formed as a function of the HBr/HCl ratio. The diagram suggests that a much higher bromine potential than chlorine potential is needed for the formation of brominated dioxin congeners. However, even in the formation region of 2,3,7,8-TeBDD, the partial pressure of HBr can be lower than that of HCl, such as is the case when HBr/HCl = 0.5. This reduced partial pressure is possible because HBr is much less thermodynamically stable than HCl, and the equilibrium of the reaction shown in Eq.3 shifts to the left. Söderström and Marklund[7,8)] have studied brominated flame retardant pyrolysis using pilot plant combustion at 1073K. They have shown that the HBr/HCl ratio in the flue gas was 0.1 for an equal amount of Br and Cl in fuel. Figure 2 shows, that under these conditions, the flue gas enters the thermodynamic region of low brominated TeXDD formation during cooling.

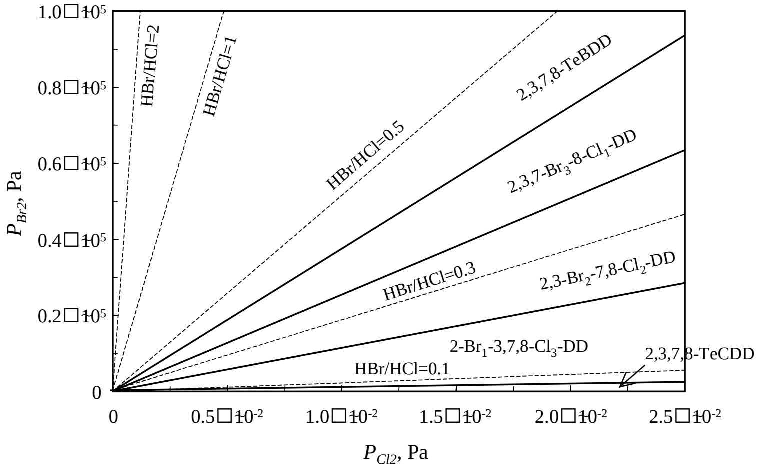

Fig.2: Bromine-chlorine equilibrium potential for the formation of 2,3,7,8-TeXDDs from 2,3,7,8-TeCDD at 573K.

Thermodynamic simulation in flue gas: Table 1 shows the input gas composition for the thermodynamic simulations, which reflects the analytical flue gas composition in flame retardant combustion.7,8)

Table 1: Input gas composition in thermodynamic simulation for formation of PXDDs.

Br + Cl	Br/Cl	O_2	H_2O
1.0×10^{-3} mol/Nm^3	0.1, 1.0, 10	10% (4.09 mol/Nm^3)	7% (2.86 mol/Nm^3)
CO_2	CO	N_2	Carbon in soot
10% (4.09 mol/Nm^3)	200ppm (8.17×10^{-3} mol/Nm^3)	73% (29.83 mol/Nm^3)	20 mol/Nm^3

Figure 3 shows the temperature changes of equilibrium amount of the bromine and chlorine gaseous species (HBr, HCl, Br, Cl, Br_2 and Cl_2) formed from the input gas at the Br/Cl ratios of 0.1, 1.0 and 10, respectively. The amounts of Br and Br_2 formed are larger than those of Cl and Cl_2 even at the Br/Cl ratio of 10, because HBr is thermodynamically much less stable than HCl.

Figure 4 shows the profile of the formed PCDD, PBDD and PXDD homologues in equilibrium at 573, 673 and 773K. The ratio of bromine to chlorine in the input gas is 1.0. The amount of dioxins formed decreases with an increase in halogenation; in addition, the amount of higher halogenated dioxins formed decrease significantly with increase in temperature. The amount of brominated dioxins formed as PBDDs and PXDDs is similar to that of the PCDDs formed, because, as shown in Fig.3, the bromine (Br_2 and Br) potentials are much higher than the chlorine (Cl_2 and Cl) potentials in the gas, even though the brominated dioxins are less thermodynamically stable than the PCDDs.

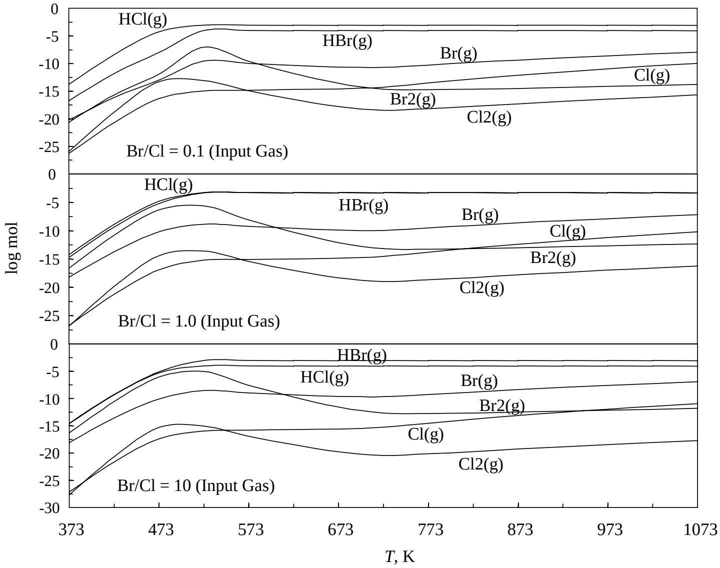

Fig.3: Temperature change in gaseous species of Br and Cl in thermodynamic simulation at Br/Cl ratios of 0.1, 1.0 and 10.

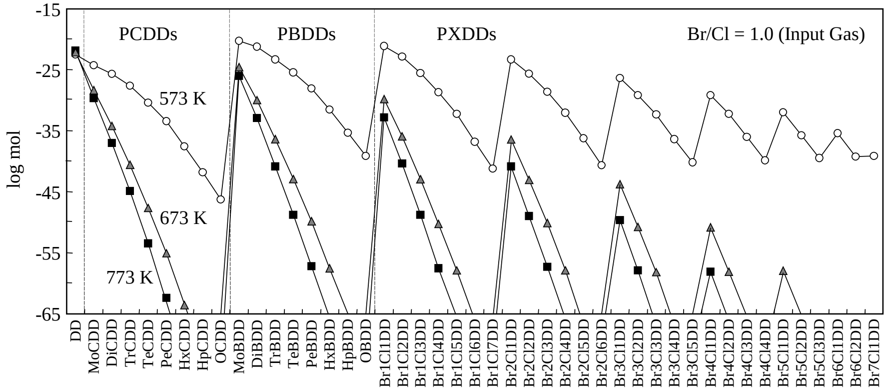

Fig.4 Profile of formed PCDDs, PBDDs and PXDDs in thermodynamic simulation at equal amount of Br and Cl at 573, 673 and 773K.

Figure 5 shows the fractions of bromine and chlorine substituted into TeBCDDs, PeBCDDs, HxBCDDs and HpBCDDs formed in the calculations. (PBCDDs means totally PCDDs, PBDDs and PXDDs.) The Br fraction describes the amount of bromine present as a proportion of total halogen (Br+Cl). The Br/(Br+Cl) fractions increase entirely with increasing in the Br/Cl ratio in the input gas. At the Br/Cl ratio of 10, the Br/(Br+Cl) fractions are almost 1.0 at the higher temperatures than 573 K. The calculated amounts of HpBCDDs at the temperatures from 773K to 1073K are too small to obtain the Br/(Br+Cl). Figure 5 shows that the Br/(Br+Cl) fractions have a trend to increase with increasing in temperature up to 573K or 673K, especially at the Br/Cl ratio of 1.0.

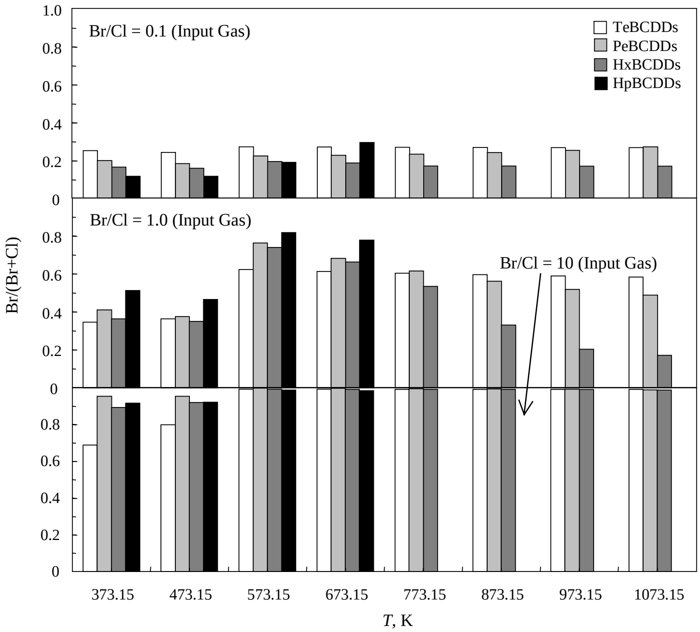

Fig.5: Fractions of bromine and chlorine substituted into TeBCDDs, PeBCDDs, HxBCDDs and HpBCDDs, respectively. The Br fraction describes the amount of bromine present as a proportion of total halogen (Br+Cl).

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