THERMODYNAMIC EVALUATION ON THE FORMATION OF DIOXINS AND COMBUSTION GAS

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Introduction

Thermodynamics of the formation and decomposition of dioxins (PCDD/Fs) in combustion gas has been discussed by the authors (1) for homogeneous gas system of C-O-H-Cl quaternary, and the effects of temperature and gas compositions have been clarified. In the present paper, the effect and mechanism of various additives (inhibitors) on the decomposition of PCDD/Fs are investigated based on this quaternary equilibria. Because of the great significance of chemical potentials such as log p_{O2}, log p_{Cl2} and log p_{H2}, the basic equilibrium relations are illustrated on the chemical potential diagrams including the carbon deposition reaction. .

Methods

Thermodynamic calculations (1) are conducted by use of HSC Chemistry (2). From the obtained results, the effects of oxygen and hydrogen on the resultant gas are shown in Figs.1 and 2 at 300° C. In the figures, the gas composition shown by an arrows is referred to the "reference gas", and the amounts of oxygen or hydrogen are increased or decreased to confirm the variation of the resulting gases. The composition of the reference gas is shown in Table 1. The abridged signs such as 4D, 4F, 8F….in the figures refer to tetra dioxin, tetra furan, octa furan, and so on. The reference gas is taken as the starting composition, and equilibrium calculations are carried out for various inhibitors added at 300° C.

Fig.1 Effect of oxygen on the formation of Fig.2 Effect of hydrogen on the formation of PCDD/Fs and principal species at 300° C.

C. PCDD/Fs and principal species at 300° C.

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Results of Equilibrium Calculation and Discussions

It should be noticed in Fig.1 or 2 that PCDD/Fs tend to decompose in both regions of rich and poor in oxygen or hydrogen. In the stable region of PCDD/Fs, chloro benzenes are always observed, but not benzene. Hydrogen and water vapor, as well as oxygen, contribute greatly to decompose PCDD/Fs and to stabilize benzene.

Fig.3 shows the calculated amounts of gas species when CaO is added to the reference gas at 300° C. As shown at the extreme left of the figure, the equilibrium amounts of furans and tetra dioxin(4D) represented by the reference gas are very large, but decrease drastically by addition of CaO more than 0.04 mol. The effect of lime on the decreases in PCDD/Fs and chlorine has been well recognized also in practice, and is explained by following reactions :

$$
CaO + 2HCl(g) = CaCl2 + H2O(g) \text{ or } CaO + Cl2(g) = CaCl2 + 0.5O2(g) \tag{1}
$$

The amount of CaCl2 is illustrated in Fig.3. From these equations, it is presumed that the decomposition of PCDD/Fs is caused by just variations in the quaternary gas composition, that is, subtraction of HCl or Cl2 and addition of H2O or O2. This presumption is confirmed by equilibrium calculation as shown in Fig.4. When corresponding amount of HCl or Cl2 is subtracted from the reference gas, and H2O or O2 is added without participation of calcium, exactly the same behavior is reproduced for the amounts of PCDD/Fs. It has been said in practice that HCl is removed from gas by CaO addition, but as shown in Eq.(1), CaO removes just Cl but remains H in gas phase; this is important to abatement of PCDD/Fs because the decrease in hydrogen in gas phase promotes the formation of PCDD/Fs. Due to the positive effect of H and O in decreasing PCDD/Fs, from thermodynamic viewpoint, Ca(OH)2 is more interesting than CaO.

Fig.3 Effect of CaO addition on the abatement Fig.4 Effect of H2O addition and HCl of PCDD/Fs to the reference gas at 300° C. subtraction to the reference gas by the . corresponding amounts.

Regarding the abatement effect of SO2 on the formation of PCDD/Fs, there exist various opinions, but the evaluation is not yet fixed (3,4). Fig.5 shows the variation of the resulting gas amounts by addition of SO2 to the reference gas. Abatement effect of SO2 is confirmed thermodynamically. As shown in the figure, the predominant sulfur-bearing species is COS at this temperature, which will be formed by following reaction :

$$
SO2(g) + 3CO(g) = COS(g) + 2CO2(g)
$$
 (2)

Instead of SO2 addition, when CO2 is added to and CO is subtracted from the reference gas by the corresponding amounts, the equilibrium calculation gives just the same amounts of PCDD/Fs with

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those in Fig.5, although sulfur is excluded from the system. Because Ca, S, H and O are efficient in decreasing PCDD/Fs, CaSO4 or CaSO4.2H2O may serve as a good inhibitor, but undoubtedly, in practical use kinetic factors or reactivity must be taken into account.

Fig.5 Effect of SO2 addition at 300° C to the Fig.6 Effect of addition of tri-ethanolamine reference gas. at 300° C to the reference gas.

It has been reported that various organic compounds are useful as inhibitors for PCDD/Fs, but any reasonable theoretical explanation has never been found. As an example, the results derived by addition of tri-ehthanolamine are illustrated in Fig.6. The main reaction will be given as follows :

 $2C6H15NO3 = N2(g) + 2C6H6(g) + 6H2O(g) + 3H2(g)$ (3)

Increases in H, O and C6H6 are convenient for the decomposition of PCDD/Fs in the quaternary gas phase. The organic compound containing high amount of H and O would be efficient in decreasing PCDD/Fs.

The inhibiting reactions were also investigated for various other substances such as NH3, sodium salts, metals, etc., and useful reports are available(5). As described above, however, in most cases the reasonable explanations are given based on the C-O-H-Cl quaternary gas equilibria. In general trends, the substance which increases oxygen and hydrogen potentials, and decreases chlorine potential is convenient as a good inhibitor for PCDD/Fs. Thus, it would be interesting to discuss the formation-decomposition equilibria by use of chemical potential diagram.

Discussions by Use of Chemical Potential Diagrams

Fig.7 shows just the same results with Fig.2,. but the ordinate is log mol% or log p , where important and basic chemical potentials are included such as $\log p_{\text{H2}}$ and $\log p_{\text{C2}}$. log p_{O2} is located at far bottom of Fig.7 at lower than –40. As an oxygen-chlorine potential diagram, log p_{O2} are plotted against log p_{C12} and the results are illustrated with FDH in Fig.8. It would be interesting that chlorine and oxygen potentials are nearly fixed (approximately, $\log p_{C12} = -11$ and $\log p_{\text{O2}} = -42$, corresponding to D) in the region where PCDD/Fs are formed. Only 8F and 8D can exist at higher $log p_{C12}$ on line DH.

In the previous report(1), the reference gas was taken as starting composition and then amounts of various gas components were changed. The results of Fig.1, where the amount of oxygen is varied, are illustrated in terms of chemical potentials with line FDO in Fig.8. Also when the amount of H2O(g) is changed, the results are just similar to FDH, but in case of Cl2(g) the results are a little different as shown with FDC. It is concluded from these results that PCDD/Fs are formed in a limited region on oxygen-chlorine potential diagram for a given starting gas containing such as 1 mol Cl shown in Table 1.

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In the above discussions, high Cl content (such as 1 mol, ca.15%) is assumed and enough chlorine remains even after formation of PCDD/Fs. However, when the level of chlorine is low as in usual combustion gas, formation of a large amount of PCDD/Fs results in exhaustion of chlorine source for other species such as HCl(g) or Cl2(g). Accordingly, the relations between log p_{02} and log *p*_{Cl2} under formation of PCDD/Fs are affected substantially by the content of chlorine in the starting gas, as shown on the left side of Fig.8. When a chlorine amount in the starting gas is smaller than 0.1 mol, chlorine potential is lowered to the direction of D' after formation of PCDD/Fs. The trends just opposite to line DH.

Fig.7 Effect of hydrogen on the composition Fig.8 Variations of log p_{O2} and log p_{C12} with of the gas phase illustrated in Fig.2. starting gas composition at 300[°]C. of the gas phase illustrated in Fig.2. starting gas composition at 300° C.

In Fig.8, PCDD/Fs are formed thermodynamically on line DD' at 300° C depending on the chlorine content. The potentials for formation of PCDD/Fs are extremely low in comparison with those reported through practical observations; it is probably for kinetic reason. The following carbon deposition reaction has usually been neglected, but must be considered in the discussion on PCDD/Fs formation (1).

$$
2CO(g) = C + CO2(g)
$$
 (4)

The potentials corresponding to carbon deposition are shown in top-left of Fig.8 with line CC'; the oxygen potential is much higher than that of PCDD/Fs formation. It is well known that Eq.4 tends to proceed to the left at high temperature forming CO rich gas. When this CO rich gas is cooled to 300° C without any composition change, the gas represents very low oxygen potential as shown at the bottom of Fig.8. The relative locations of these oxygen potentials look interesting in the estimation of the formation mechanism of PCDD/Fs, but careful combination with kinetic aspects must be indispensable for explanation of practical observations.

Thermodynamic evaluation on the C-O-H-Cl quaternary gas is very useful for prediction of behavior of PCDD/Fs formation, but the reliability depends on the precision of the free energy data. Moreover, the reaction must be very slow at the relevant low temperature, and thus the practical system must be far from the equilibrium. Accordingly, the numerical values derived above are meaningless to compare with practical ones, but the obtained trends will be helpful for understanding the behavior of PCDD/Fs.

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