ISOMER PREDICTION MODEL OF POLYCHLORINATED DIBENZOFURANS FROM MUNICIPAL WASTE INCINERATORS

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Introduction

The isomer patterns of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) from municipal waste incinerators (MWIs) are known to be consistent[1] with some exceptions.[2] Addink et al.[3] investigated the similarity of the isomer patterns between a field sample and equilibrium concentrations predicted from calculated Gibbs free energy of formation ($\Delta G°_{f,T}$) values,[4] relative to each total homologue. However, it was not confirmed that the sampled isomer patterns were thermodynamically controlled, and the question that still remains to be answered is what mechanism causes the similarity of the PCDD/F isomer patterns in these different kinds of incinerators under different combustion conditions?
The possibility that PCDD/F isomer patterns shown in field data can be explained, in part, by dechlorination kinetics was explored by Wiesmüller[5]. In his model, however, all reaction kinetic constants of chlorination and dechlorination of each PCDD/F isomer were considered to solve partial differential equations for the isomer patterns. This current work proposes a conceptual theory to model isomer patterns that is useful in understanding PCDD/F formation mechanisms.

Methods

In this research we attempted to predict the field-sampled isomer patterns of PCDFs by assuming that the measured chromatograph peak areas of the four heptachloro-dibenzofuran (H7CDF) isomers, relative to the total H7CDFs, are determined by position-specific dechlorination kinetics from an octachloro-dibenzofuran (O8CDF) parent, and that these probabilities can subsequently predict the relative concentrations of lower chlorinated isomers such as hexachloro-dibenzofurans (H6CDFs) and further still to the pentachloro-dibenzofurans (P5CDFs), etc. When the relative peak area ratios of 1,2,3,4,6,7,8-, 1,2,3,4,6,7,9-, 1,2,3,4,6,8,9-, and 1,2,3,4,7,8,9-H7CDFs are termed a, b, c, and d, respectively, in the typical H7CDF chromatograms of field samples, the predicted concentration of each isomer in H6CDFs, P5CDFs, and T4CDFs can be expressed by the four constants (a, b, c, and d) and the number of dechlorination pathways to the isomer. Those values show only the isomer contents in a homologue; they don't represent the quantitative relation between homologues. The values of a, b, c, and d are the dechlorination probabilities from the 9- or 1-, 8- or 2-, 7- or 3-, and 6- or 4-substitution positions, respectively, on a PCDF molecule. The predicted results were calculated with a=0.630, b=0.166, c=0.129, and d=0.0755 which were obtained from typical MWI samples. Prediction of PCDD isomer patterns was also attempted according to the same principle. The prediction equations for PCDD isomers are shown in Table 1. (The predicted PCDD isomer patterns did not fit the field isomer patterns.) The

coefficient of each equation in Table 1 represents the number of dechlorination pathways. The more symmetrical isomer has smaller coefficients due to fewer possible dechlorination pathways.

Table 1. The predicted peak ratios of H6CDDs, P5CDDs, and T4CDDs, with a and b as the relative peak ratios of the two H7CDDs, respectively.

isomers	equations	isomers	equations
H7CDDs		1,2,4,6,7-	$6ab^2$
1,2,3,4,6,7,8-	a	1,2,4,8,9-	$6ab^2$
1,2,3,4,6,7,9-	b	1,2,3,4,6-	$6ab^2$
		1,2,3,6,7-	$6a^2b$
H6CDDs		1,2,3,8,9-	$6a^2b$
1,2,4,6,7,9-/1,2,4,6,8,9-/1,2,3,4,6,8-	b^2+b^2+2ab		
1,2,3,6,7,9-/1,2,3,6,8,9-	2ab+2ab	T4CDDs	
1,2,3,4,7,8-	a^2	1,3,6,8-	$12a^2b^2$
1,2,3,6,7,8-	a^2	1,3,7,9-	$12a^2b^2$
1,2,3,4,6,9-	b^2	1,3,7,8-	$24a^3b$
1,2,3,7,8,9-	a^2	1,3,6,9-/1,2,4,7-/1,2,4,8-	$24ab^3+24a^2b^2+24a^2b^2$
1,2,3,4,6,7-	2ab	1,2,6,8-	$24a^2b^2$
		1,4,7,8-	$12a^2b^2$
P5CDDs		2,3,7,8-	$6a^4$
1,2,4,6,8-/1,2,4,7,9-	$6ab^2+6ab^2$	1,2,3,7-	$24a^3b$
1,2,3,6,8-	$6a^2b$	1,2,3,4-/1,2,4,6-/1,2,3,8-/1,2,4,9-	$12a^2b^2+24ab^3+24a^3b+24ab^3$
1,2,4,7,8-	$6a^2b$	1,2,3,6-/1,2,7,9-	$24a^2b^2+24a^2b^2$
1,2,3,7,9-	$6a^2b$	1,4,6,9-/1,2,7,8-	$6b^4+24a^3b$
1,2,4,6,9-/1,2,3,4,7-	$6b^3+6a^2b$	1,2,3,9-	$24a^2b^2$
1,2,3,7,8-	$6a^3$	1,2,6,9-	$24ab^3$
1,2,3,6,9-	$6ab^2$	1,2,6,7-	$12a^2b^2$
		1,2,8,9-	$12a^2b^2$

Results and Discussion

In Figure 1, the predicted H6CDF isomers (blank bar) are compared with those of the eight field fly ash samples (filled bar) which were randomly collected from eight MWIs in Japan. The field samples are numbered 1 to 8 (1 to 4: fluidized bed incinerators; 5 to 8: stoker type incinerators) from left to right for each isomer. The predicted isomer patterns of H6CDFs (Fig.1) and P5CDFs show almost identical isomer patterns with the MWIs. The T4CDF isomer pattern was only fairly well predicted. Agreement between the model and sampled data is consistent with formation of T4CDFs to H7CDFs by dechlorination from an O8CDF parent.

The isomer pattern (slant-line bar) obtained from an experiment with graphite and CuCl at 500 ℃[6] is also compared in Fig. 1. The isomer pattern was remarkably similar to the predicted except for 2,3,4,6,7,8-H6CDF, which was substantially lower than the predicted. The formation mechanism of PCDFs from graphite and CuCl may be the same as those in MWIs.

As an evaluating method of isomer pattern matching, Morita et al.[7] introduced similarity, S, as:

$$S = \frac{\sum A_i B_i}{\sqrt{\sum (A_i)^2 \sum (B_i)^2}}$$

where A_i and B_i are the homologue-normalized isomer contents of the isomer *i* in samples A and B, respectively. The $S_{IIG}(n)$ (number of samples, n =1 to 8) values between the predicted isomer contents in this paper and the MWI samples n are shown in Table 2. Likewise, $S_{IIG}(e)$ shows the

similarity between the predicted and the equilibrium isomer concentrations. IIG was taken from Iino-Imagawa-Gullett.

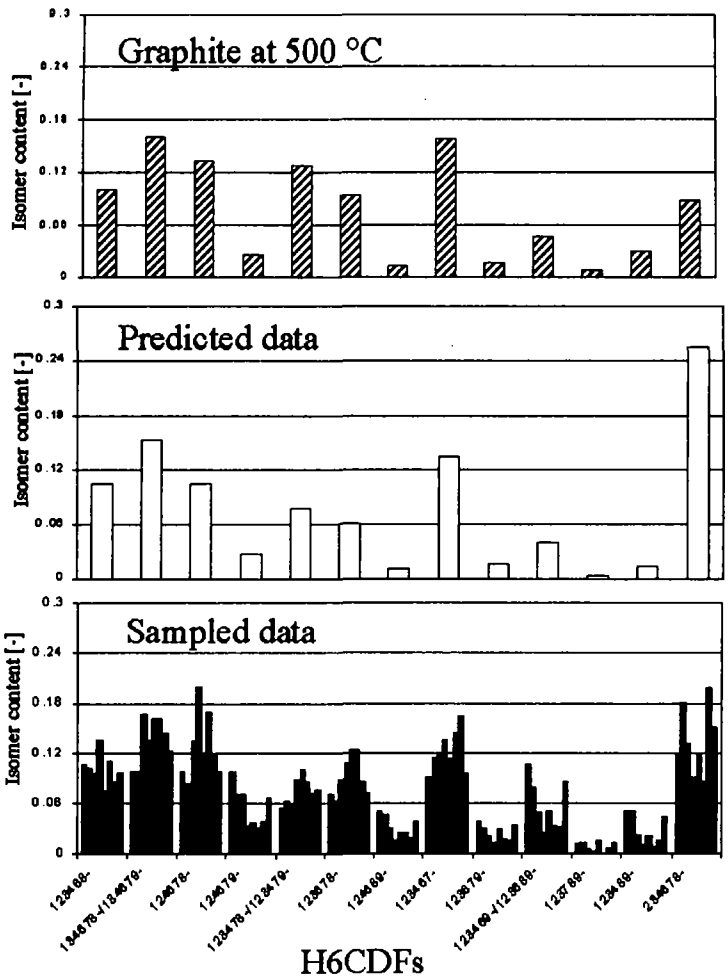

Fig. 1 H6CDF isomer patterns from graphite/CuCl at 500 °C, dechlorination model, and eight field samples

The $S_{IIG}(n)$ of H6CDFs, P5CDFs, and T4CDFs between the predicted and MWI samples are within 0.98 to 0.85, 0.96 to 0.79, and 0.92 to 0.70, respectively. These values indicate that the data are well-predicted by the dechlorination-controlled isomer patterns. The decreasing $S_{IIG}(n)$ with the lower degree of chlorination can be attributed to two possible reasons. One reason is that the error which derives from the assumption of constant position-specific dechlorination probabilities propagates every time in multiplying the probability to get lower chlorinated PCDFs. The dechlorination probability from a position on a PCDF molecule may be different before and after dechlorination occurs at other positions. The other possible reason is that different formation mechanisms are controlling the lower chlorinated PCDFs such as chlorination from further lower chlorinated PCDFs and *de novo* synthesis from polycyclic aromatic hydrocarbons[8].

Similarity calculations with the dechlorination model and the equilibrium models result in $S_{IIG}(e)$ of P5CDFs and T4CDFs that are 0.45 and 0.48, respectively, from which it can be concluded that the predicted and the equilibrium concentrations do not have similar patterns.

Table 2. Calculated values of similarity, S. $S_{DG}(n)$ shows similarity between the predicted distributions and eight samples from eight MWIs in Japan, and $S_{NG}(e)$ between the predicted and the equilibrium concentrations calculated from dG.

	H6CDF	P5CDF	T4CDF
$S_{IIG}(1)$	0.86	0.94	0.88
$S_{IIG}(2)$	0.95	0.93	0.80
$S_{IIG}(3)$	0.93	0.95	0.89
$S_{IIG}(4)$	0.94	0.96	0.92
$S_{IIG}(5)$	0.85	0.79	0.79
$S_{IIG}(6)$	0.91	0.82	0.70
$S_{IIG}(7)$	0.86	0.81	0.80
$S_{IIG}(8)$	0.98	0.93	0.89
$S_{IIG}(e)$	0.70	0.45	0.48

The buildup of PCDF isomer patterns was also attempted on the assumption that four monochlorodibenzofurans are formed by chlorination from dibenzofuran, but no significant results were found. This suggests that dechlorination mechanisms are better able to explain these field results than mechanisms of chlorination from lower chlorinated isomers.

The predicted PCDD isomer patterns were compared with those from the field samples. The prediction did not seem to fit well, which implies existence of other predominant formation mechanisms as pointed out by Wehrmeier et al.[9].

The successful prediction of the PCDF isomer patterns leads to an equation to predict 2,3,7,8-T4CDD toxic equivalent (TEQ) values from homologue profiles as follows:

$$TEQ_{IIG} = 0.0001 \times H_8 + 0.01 \times \frac{(a+d)}{T_7} \times H_7 + 0.1 \times \frac{(2ad + 2ad + d^2 + a^2)}{T_6} \times H_6 + (0.05 \times \frac{6ad^2}{T_5} + 0.5 \times \frac{6a^2d}{T_5}) \times H_5 + 0.1 \times \frac{12a^2d^2}{T_4} \times H_4$$

where $H_{8\text{-}4}$ are concentrations of each homologue of O8CDF to T4CDF and $T_{8\text{-}4}$ are the sum of the prediction equations for each isomer. Toxic equivalent factors (TEF) determined by the World Health Organization[10] were used. The statistical evaluation of this model is a future work. These equations in this dechlorination model may be important in the near future to support real-time measurements of PCDD/Fs by the resonance-enhanced multiphoton ionization (REMPI) method.

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