

ISOMER PATTERN PREDICTION OF PCDFs, PCDDs, PCNs, AND PCBs FROM MUNICIPAL WASTE INCINERATORS AND CALCULATION OF TETRACHLORONAPHTHALENE EQUILIBRIUM DISTRIBUTIONS

Fukuya Iino[†]*, Kentaro Tsuchiya¹*, Takashi Imagawa¹, and Brian K. Gullett

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, MD-65, Research Triangle Park, NC 27711, USA

¹National Institute for Resources and Environment, Tsukuba, Ibaraki 305-8569, Japan

[†] Joint program with Oak Ridge Institute for Science and Education postdoctoral research program.

* The present addresses are Research Center for Chemical Risk Management (F. Iino) and Research Institute of Energy Utilization (K. Tsuchiya), National Institute of Advanced Industrial Science and Technology, Onogawa 16-3, Tsukuba, Ibaraki 305-8569, Japan

Introduction

Isomer pattern prediction of polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzo-*p*-dioxins (PCDDs) from municipal waste incinerators (MWIs) was attempted by a model based on the N-1 chlorinated isomer patterns (N = the number of chlorine atoms of the fully chlorinated species)^{1,2}. In order to predict the isomer patterns, constants representing the relative N-1 chlorinated species concentrations, such as **a**, **b**, **c**, and **d** for heptachlorodibenzofurans (H7CDFs), are derived from one or two typical stoker-type MWI isomer patterns of the N-1 chlorinated species [H7CDFs, heptachlorodibenzo-*p*-dioxins (H7CDDs)]. The predicted results were compared with other field data collected from MWIs in Japan. The prediction of PCDFs showed an excellent fit to the field fly ash data from the eight MWIs in Japan¹. The PCDD prediction was not successful².

In this current work, we modify the previous theory to view the coefficients and the constants (**a**, **b**, **c**, and **d**) of the prediction equations as inversed symmetric number of each isomer and the chlorination preference for their respective positions, respectively. The modified conceptual theory was also applied to polychlorinated naphthalenes (PCNs) and polychlorinated biphenyls (PCBs), and the predicted isomer patterns are compared with those from MWIs in Japan. Thermodynamic equilibrium isomer patterns of tetrachloronaphthalenes (TeCNs) were obtained by *ab initio* quantum mechanical calculations. The similarity values³ between the predicted, the sampled, and the equilibrium isomer patterns of TeCNs were calculated in order to validate this model.

Prediction Models and Calculation Methods

In this revised Iino-Imagawa-Gullett (IIG) model, the equations of PCDFs, for example, can be formatted as:

$$\frac{1}{\sigma} a^w b^x c^y d^z \quad (1)$$

where σ is a symmetric number (the number of indistinguishable orientations of a molecule) for each isomer and the inversed symmetric number was discussed by Bishop and Laidler⁴. Note that Eqn. (1) can be used to derive relative intrahomologue concentrations either from chlorination of the monochlorodibenzofurans (M1CDFs) to the O8CDF, or vice versa. While the equations and

the values of **a**, **b**, **c**, and **d** changed from those previously reported for PCDD/Fs, the relative concentration values remain the same as in Refs. 1 and 2.

PCN isomer patterns were predicted by the same theory as the Eqn. (1). The relative peak ratios of the 1,2,3,4,5,6,7- (IUPAC #73) and 1,2,3,4,5,6,8-HpCNs (#74) are termed **a** and **b** which correspond to the dechlorination from the α positions (1-, 4-, 5-, or 8-) and β positions (2-, 3-, 6-, or 7-), respectively, on a PCN molecule. The values of $a=0.828$ and $b=0.172$ were taken from the relative abundance of each isomer in a representative MWI sample.

The nonachlorobiphenyl (NoCB) isomers of IUPAC #206, #207, and #208 correspond to dechlorination at the 2- or 6-position, 3- or 5-position, and 4-position from decachlorobiphenyl (DeCB, #209), respectively. The values used for the PCB prediction were $a=0.556$ for #206, $b=0.253$ for #207, and $c=0.192$ for #208.

In order to calculate the equilibrium TeCN isomer pattern, the relative energies of the 22 TeCN isomers were obtained by using Gaussian 98 code⁵. The G3(MP2)//B3LYP composite method⁶ was employed in order to estimate enthalpies and $\Delta G_{f,T}^\circ$ at 298.15, 573, and 1073K, respectively, for all 22 TeCN isomers.

Results and Discussion

Fly ash samples were collected from 3 types of 12 MWIs. The MWIs are continuous stoker types (A to C), mechanical batch stoker types (D and E), and fluidized bed incinerators (F to L). In the hexachloronaphthalene (HxCN) shown in Fig. 1 and pentachloronaphthalene (PeCN) homologues, the

predicted isomer patterns are fairly similar to stoker type incinerator patterns (A to E) and to some of the fluidized bed incinerators (F and G). For MWIs H to L, 1,2,3,4,5,6-HxCN (#63) and coeluting 1,2,4,7,8- (#62) and 1,2,3,4,5-PeCNs (#49) showed remarkable differences from those in the stoker type patterns. Imagawa and Lee⁷ pointed out that these isomers might be caused by preferentially oriented chlorination. In the TeCN homologue, the model prediction is not completely successful except for MWIs A and C. In particular, 1,3,6,7- (#44) and a coeluted peak of 2,3,6,7-/1,2,6,8-TeCNs (#48/40) are marginally predicted for all of the field samples.

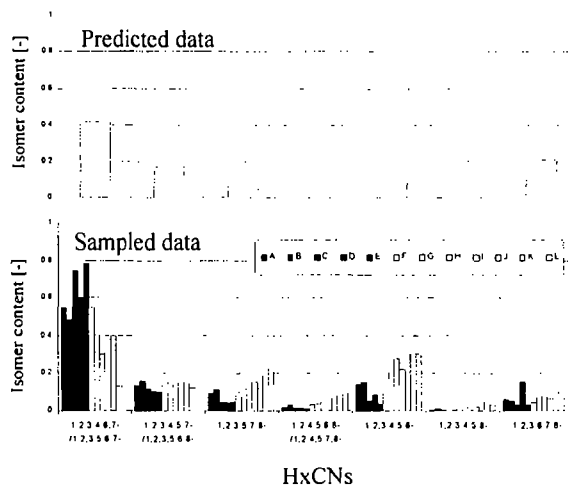


Fig. 1 Predicted HxCN isomer pattern and the 12 MWI sampled data.

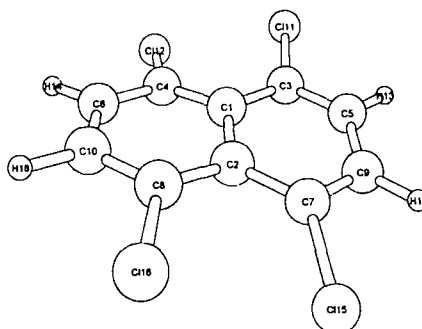


Fig. 2 Structure of 1,4,5,8-TeCN

In the process of optimizing the TeCN molecules' geometry, which is necessary in order to calculate thermodynamic properties, it was found that 1,4,5,8-TeCN (#46) has a non-planar structure (Fig. 2). Significant disruption of the coplanar nature of the 1,4,5,8-TeCN (#46) isomer as well as OcCN (#75) was also concluded by Kalmykova et al. with infrared (IR) spectra⁸. At 298.15 and 573K, 1,3,5,7-TeCN (#42) is the most stable because chlorine atoms are in the least crowded positions, and the distortion of the 1,4,5,8-TeCN (#46) isomer makes it the most thermodynamically unstable at all three temperatures (Fig. 3). At temperatures considered optimum for post-combustion formation of PCDD/Fs and PCNs via precursor condensation or *de novo* formation, 573K, 1,3,5,7-TeCN (#42) therefore is the most prevalent TeCN isomer. At 1073K, within the temperature range of combustion chamber outlets, the equilibrium isomer concentrations are the most broadly distributed, and this TeCN equilibrium isomer pattern at 1073K was compared with the sampled TeCN data.

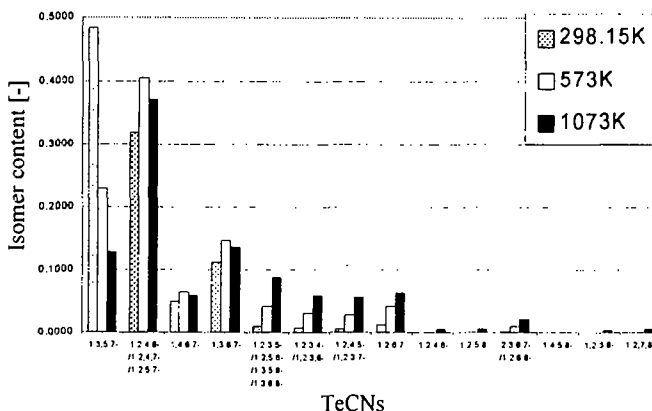


Fig. 3 Equilibrium TeCN isomer patterns at 298.15, 573, and 1073K.

The field samples, which showed similarity values, $S_{eq}(n)$ of more than 0.70, were only C (0.72), F (0.79), and H (0.82), and no consistent similarity values can be seen in the same category of MWIs. Therefore, we concluded that the TeCN isomers emitted from MWIs are not in equilibrium. Similarity values, $S_{IIG}(n)$, of more than 0.81 clearly support the observation that the IIG-model-predicted results for HxCNs and PeCNs matched well with all of the investigated stoker type incinerators (A to E) and some fluidized bed incinerators (F and G). In the TeCNs, the worst $S_{IIG}(n)$ is 0.45 for sample B, yet more than 0.70 for A and C to G. The IIG-model prediction was not perfectly successful for the TeCNs.

Two field isomer patterns of PCBs were measured from two stoker-type MWI samples that were taken in Japan from one emission gas sample (sample X) and one fly ash sample (sample Y). Both MWIs have a maximum capacity of 200 Mg/day of municipal solid waste and an electrostatic precipitator as a dust collector⁹. The cleanup and analytical methods are described in detail elsewhere¹⁰. The isomer patterns of octachlorobiphenyls (OcCBs) and heptachlorobiphenyls (HpCBs) shown in Fig. 4 were reasonably well predicted with S values of more than 0.84. $S_{IIG}(X)$ and $S_{IIG}(Y)$ are 0.88 and 0.91 for OcCBs and 0.88 and 0.84 for HpCBs, respectively. However,

Table 1. Calculated values of similarity, S for PCNs.

Similarity values between equilibrium and samples	TeCN	Similarity values between prediction and samples	HxCN	PeCN	TeCN
$S_{eq}(A)$	0.67	$S_{IIG}(A)$	0.94	0.87	0.81
$S_{eq}(B)$	0.44	$S_{IIG}(B)$	0.94	0.88	0.45
$S_{eq}(C)$	0.72	$S_{IIG}(C)$	0.89	0.86	0.82
$S_{eq}(D)$	0.51	$S_{IIG}(D)$	0.96	0.89	0.73
$S_{eq}(E)$	0.61	$S_{IIG}(E)$	0.88	0.86	0.70
$S_{eq}(F)$	0.79	$S_{IIG}(F)$	0.93	0.82	0.73
$S_{eq}(G)$	0.54	$S_{IIG}(G)$	0.93	0.81	0.71
$S_{eq}(H)$	0.82	$S_{IIG}(H)$	0.85	0.54	0.53
$S_{eq}(I)$	0.47	$S_{IIG}(I)$	0.88	0.63	0.59
$S_{eq}(J)$	0.42	$S_{IIG}(J)$	0.93	0.74	0.61
$S_{eq}(K)$	0.34	$S_{IIG}(K)$	0.64	0.30	0.43
$S_{eq}(L)$	0.33	$S_{IIG}(L)$	0.62	0.35	0.47

$S_{eq}(A)$: Similarity between equilibrium at 1073K and sampled data A

$S_{IIG}(A)$: Similarity between prediction and sampled data A

A to C: Stoker type incinerators

D and E: Mechanical batch stoker type incinerators

F to L: Fluidized bed incinerators

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since a model, in which the a, b, and c constants are taken from the monochlorobiphenyl (MoCB) isomer patterns, showed the similar tetrachlorobiphenyl (TeCB) isomer patterns to those predicted by the model based on the NoCB isomer pattern, further investigation is necessary to determine the most appropriate model for PCBs.

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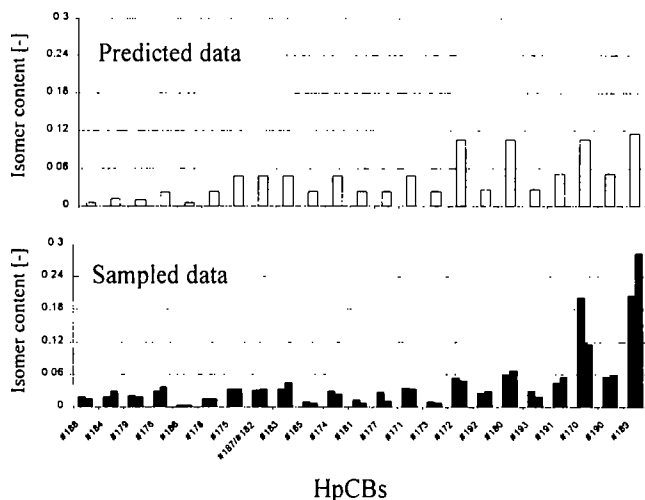


Fig. 4 Predicted HpCB isomer pattern and the two sampled data

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