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# Isomer Distributions of Polychlorinated Dibenzo-*p*-dioxins/ Dibenzofurans Formed during De Novo Synthesis on Incinerator Fly Ash

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Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) emitted from municipal waste incinerators appear to have a chlorination pattern that is quite constant across various samples and conditions. This suggested that these patterns may be controlled by thermodynamic properties of the individual PCDD/F congeners, such as the free Gibbs energy of formation ($\Delta G°_{f,T}$). This would make prediction of the isomer composition of a particular sample (and hence its TEQ value) possible, based on values of $\Delta G°_{f,T}$. A laboratory scale study was carried out with activated carbon on fly ash as the source of PCDD/F formation. Although it was found that the isomer distributions within homologues were independent of the reaction time (proof of thermodynamic control), other observations (lack of equilibrium/isomerization between isomers and lack of similarity between isomer distributions measured and predicted by $\Delta G°_{f,T}$) contradicted the possibility of thermodynamic control. Hence, this study could not confirm that de novo formation of PCDD/F could explain thermodynamically controlled isomer distributions in incinerators. Some recommendations for further work—time-based studies with precursors, isomerization studies with single congeners, and more data on $\Delta G°_{f,T}$ values of PCDD/F—were made.

## Introduction

Formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) during municipal waste incineration was discovered in 1977 (*1*). The presence of these compounds on incinerator fly ash has led to laboratory-scale modeling of the formation process. Recent reviews summarized the most important trends and results (*2*, *3*).

One striking aspect of the formation of PCDD/F was the similarity of the isomer distributions within homologues that was usually found in various waste incinerator fly ashes (*4*). Given the large variety of reaction conditions that must exist (e.g., feed, residence time, temperature), this observation suggested that the final distributions within homologues would be governed by thermodynamic properties of the individual PCDD/F isomers. A distribution that was very dependent on kinetic parameters would more likely differ between incinerators. Knowledge of the factors that determine the isomeric composition of PCDD/F effluents is crucial, since the TEQ value of a specific emission depends on the presence of the 2,3,7,8-substituted congeners.

Values of $\Delta H°_{f,T}$ and $\Delta G°_{f,T}$ for the various PCDD/F congeners were reported by a number of authors (*5*−*11*). These thermodynamic data could then be used to compare isomer distributions measured in effluents and predicted by theory. Typical isomer distributions within homologues from various combustion sources showed a certain degree of similarity with predictions based on values of $\Delta G°_{f,T}$, although results differed per homologue (*8*, *11*).

The concept of thermodynamic control of PCDD/F isomer distributions within homologues required more proof than a correlation between isomer distributions measured (in real incinerators) and predicted by values of $\Delta G°_{f,T}$. In addition, time independence of the distributions and the existence of some kind of equilibrium between the isomers (e.g., through isomerization) would have to be verified. Both the influence of time and possible equilibration could be studied readily on a laboratory scale. The small scale offered the advantage of better control of reaction conditions. For instance, a time study in a municipal waste combustor would be more difficult, since the fly ash sampled for several hours would have a poorly defined time history.

We carried out a series of experiments to investigate to what extent the isomer distributions of PCDD/F within homologues were thermodynamically controlled. We chose carbon as the reactant in this study since de novo formation of PCDD/F is a slow process (hours), which made it possible to vary the reaction time over a wide range. Time, temperature, [$H_2O$], [HCl], and [$O_2$] were varied to study the influence of these parameters on the isomer distributions. Time dependence of the isomer distributions, the extent to which equilibrium exists, and a comparison between isomer distributions measured and predicted are reported.

## Experimental Section

Experimental conditions are described in Table 1. Details on apparatus, mixing and heating, cleanup, and analysis were described as follows: set 1 in ref *12*, set 2 in ref *13*, set 3 in ref *14*, set 4 in ref *15*, set 5 in ref *15*, and set 6 in ref *16*. All experiments were carried out with a mixture of activated carbon and fly ash from a municipal waste incinerator in Zaanstad, The Netherlands. All native organic material had been removed from the fly ash before mixing it with the activated carbon. All runs were carried out with the mixture placed as a fixed bed in a glass/quartz tube that was heated in a furnace. A gas stream passed through the fly ash bed during all experiments, except in set 2. Evaporated PCDD/F were collected in a cold trap. PCDD/F from the fly ash and cold trap were combined in the sample cleanup. $T_4$CDD-OCDD and $T_4$CDF-OCDF were quantified on a GC/MS with a SP 2331 column. This column separated the 134 tetra−hepta congeners into 102 peaks, giving a detailed picture of the isomer distributions within the homologues (*16*). All experiments were carried out twice.

## Results and Discussion

As can be seen in Table 1, we carried out six sets of experiments. Since data on the amount of PCDD/F, [PCDD]:[PCDF] ratios, and homologue distributions have been

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**TABLE 1. Reaction Conditions Used in the Experiments**

set 1: variation of reaction time
4.0 g of 97.5% fly ash and 2.5% carbon; $T = 300$ °C; 30, 60, 120, 240, or 360 min; 17 mL/min technical air; $H_2O$ added by passing flow through impinger, but not quantified
set 2: variation of reaction time
2.0 g of 98% fly ash and 2% carbon; $T = 348$ °C; 50, 110, or 230 min; no flow through the fly ash bed
set 3: variation of temperature
2.0 g of 93% fly ash, 2% carbon and 5% NaCl; $T = 298$, 348, or 398 °C; 60 min; $N_2$ 53 mL/min, $O_2$ 6.5 mL/min; $H_2O$ added by passing flow through impinger, but not quantified
set 4: with and without water
2.0 g of 98% fly ash and 2% carbon; $T = 348$ °C; 60 min; $N_2$ 103 mL/min, $O_2$ 12 mL/min, $H_2O$ (vapor) 0 or 27 mL/min
set 5: with and without HCl
2.0 g of 98% fly ash and 2% carbon; $T = 348$ °C; 60 min; $N_2$ 103 mL/min, $O_2$ 12 mL/min or $N_2$ 99 mL/min, $O_2$ 12 mL/min, HCl 0 or 5 mL/min
set 6: variation of percentage of $O_2$
2.0 g of 96.4% fly ash, 1.5% carbon and 2.1% NaCl; $T = 348$ °C; 50 min; $N_2$ 200−207 mL/min, $O_2$ 2, 4, 10, or 20 mL/min

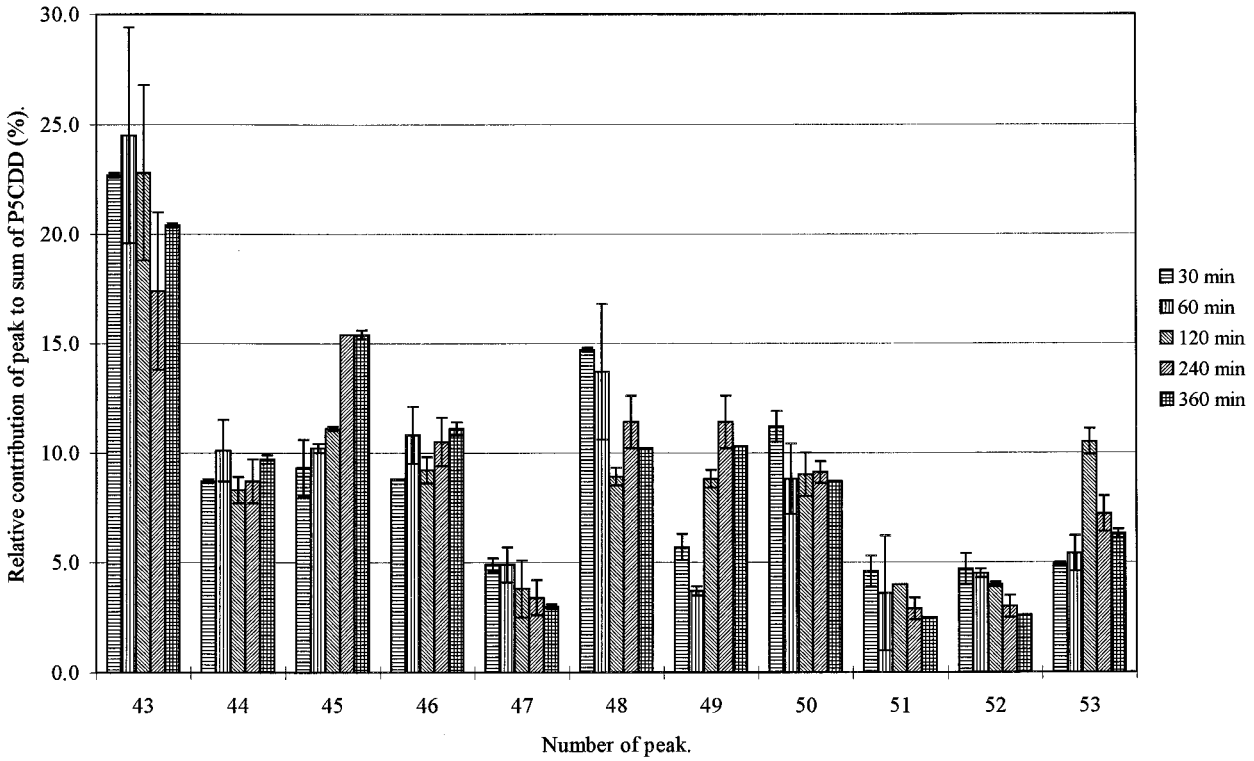


**FIGURE 1. $P_5$CDD isomer distribution for set 1. Explanation of peak numbers: 43 = 1,2,4,7,9 + 1,2,4,6,8; 44 = 1,2,3,6,8; 45 = 1,2,4,7,8; 46 = 1,2,3,7,9; 47 = 1,2,4,6,9 + 1,2,3,4,7; 48 = 1,2,3,7,8; 49 = 1,2,3,6,9; 50 = 1,2,4,8,9 + 1,2,4,6,7; 51 = 1,2,3,4,6; 52 = 1,2,3,6,7; 53 = 1,2,3,8,9.**

described elsewhere (*12*−*15*), we focused in this paper on the isomer distributions produced in these experiments. Sets 1 and 2 were designed to study the influence of the reaction time on the isomer distributions. In set 2, no flow was present during the experiments, the bed was heated in an open tube, and $O_2$ could enter by diffusion as described elsewhere (*13*). Figure 1 depicts the influence of time on the $P_5$CDD distribution in set 1. The peak numbers on the horizontal axis refer to the elution order of the various isomers on the SP 2331 GC column. Note that not all isomers could be separated due to coelution. For each experiment within a set, all the homologue distributions were calculated by setting the sum of each homologue to 100% and calculating the relative contribution of each peak. The mean values for the $P_5$CDD homologue of set 1 are shown in Figure 1, the error bars representing the range. The trend found was that the $P_5$CDD isomer distribution was independent of the reaction time. Differences found as result of increasing reaction times were small and in the same order of magnitude as the variation between duplicate experiments. Similar results were found for all other homologues in both sets 1 and 2 (not shown). The shortest time used was 30 min (set 1). Shorter reaction times were difficult with de novo type reactions since short time scale runs produced too little PCDD/F.

The time independence of PCDD/F formation (from carbon) suggested thermodynamic control of the isomer distributions, although nothing could be said about reaction times <30 min. If the isomer distributions were thermodynamically controlled, some kind of equilibrium/steady state had to exist. This would be the case if isomerization of PCDD/F after formation was fast relative to other reactions, creating an equilibrium between all possible substitution patterns within a homologue. We investigated this possibility by reacting 1,2,3,4,7,8-$H_6$CDD on fly ash. However, no isomerization was observed. Also, the dechlorination products of this particular isomer—$T_4$CDD and $P_5$CDD isomers—did not isomerize. A more detailed account of these experiments was given in ref *17*. The absence of isomerization with this single $H_6$CDD compound suggested that isomerization of PCDD/F after formation was not an important pathway on this fly ash. Therefore, no equilibrium through isomerization would exist. These observations

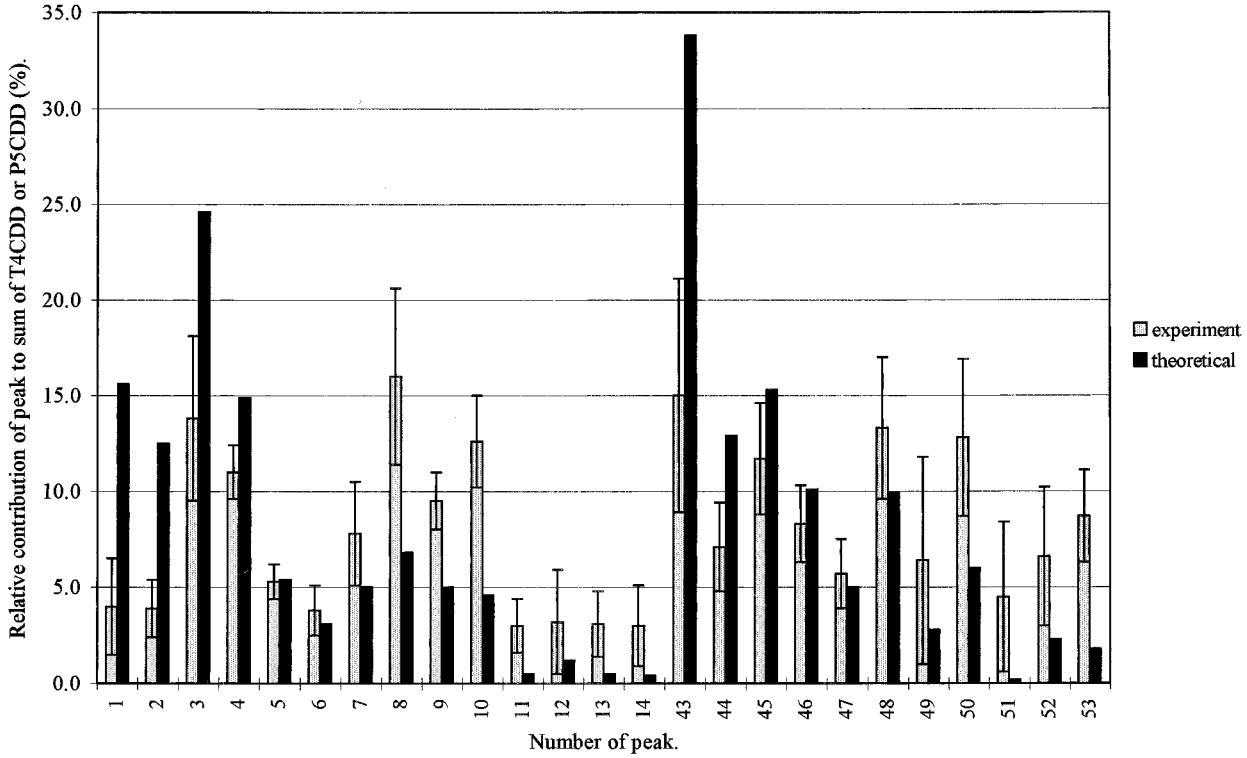


**FIGURE 2. Experimental and theoretical values for $T_4$CDD and $P_5$CDD isomer distribution. Explanation of peak numbers: $T_4$CDDs (peaks 1−14): 1 = 1,3,6,8; 2 = 1,3,7,9; 3 = 1,3,7,8; 4 = 1,3,6,9 + 1,2,4,7 + 1,2,4,8; 5 = 1,2,6,8; 6 = 1,4,7,8; 7 = 2,3,7,8; 8 = 1,2,3,4 + 1,2,3,7 + 1,2,3,8 + 1,2,4,6 + 1,2,4,9; 9 = 1,2,3,6 + 1,2,7,9; 10 = 1,2,7,8 + 1,4,6,9; 11 = 1,2,3,9; 12 = 1,2,6,9; 13 = 1,2,6,7; 14 = 1,2,8,9. $P_5$CDDs (peaks 43−53): 43 = 1,2,4,7,9 + 1,2,4,6,8; 44 = 1,2,3,6,8; 45 = 1,2,4,7,8; 46 = 1,2,3,7,9; 47 = 1,2,4,6,9 + 1,2,3,4,7; 48 = 1,2,3,7,8; 49 = 1,2,3,6,9; 50 = 1,2,4,8,9 + 1,2,4,6,7; 51 = 1,2,3,4,6; 52 = 1,2,3,6,7; 53 = 1,2,3,8,9.**

formed an argument against thermodynamic control of isomer distributions during de novo formation on our fly ash.

Experiments carried out in sets 3−6 (Table 1) were aimed at studying the influence of parameters other than time on the isomer distributions within homologues. We varied temperature, [$H_2O$], [HCl], and [$O_2$]. The results of these experiments were obvious: little variation was seen in the isomer distributions (not shown, calculated in the same manner as the distributions in Figure 1). Since no particular reaction parameter influenced the isomer patterns, we decided to calculate the average value for each peak over all experiments in all sets. Results are shown in Figures 2−6. For peak 1 in Figure 2, representing 1,3,6,8-$T_4$CDD, 26 values from each experiment in sets 1−4 were averaged. For this peak, the values in sets 5 and 6 were not available, since the formation of $T_4$CDD in these experiments was too low, perhaps due to increased levels of chlorine favoring formation of higher chlorinated congeners (set 5) or decreased $O_2$ (set 6). The error bars represent the standard deviation. The average percentage ± standard deviation shows the natural boundaries of this particular isomer on the fly ash used. For all isomers, the standard deviation varied between 10 and 300% relative to the average percentage, with an average of 50%.

The theoretical values depicted in Figures 2−6 were based on calculations of $\Delta G°_{f,T}$ for all tetra−hepta CDD/F. Calculations by Thompson (*9*, *10*) and Unsworth et al. (*8*) gave values of $\Delta G°_{f,T}$ that were quite comparable. Also, the values of $\Delta G°_{f,T}$ within a certain homologue were quite close for all isomers within that homologue. Those reported by Shaub (*5*−*7*) showed large variations within homologues, which seemed unrealistic for a set of isomers. We therefore decided to use the data reported in ref *8* and additional data made available to us based on the same technique (*18*). We assumed 600 K as the average temperature of our experiments. With all $\Delta G°_{f,600K}$ values for the isomers within a homologue available, the equilibrium composition, assuming isomerization between all the isomers, could be calculated (*8*). As with the experimental isomer distributions, the sum of the homologue was set to 100%, and all relative contributions were determined. The variation of the theoretical isomer distributions within the temperature range of our experiments was negligible. When a peak represented more than one isomer in Figures 2−6, their theoretical values were added to make a direct comparison with the experimental value possible.

If our experimental and theoretical isomer distributions would be (very) similar, this would constitute an important argument in favor of thermodynamic control of these distributions during de novo formation. The theoretical approach showed that with thermodynamic control all PCDD/F congeners were formed. There would be no homologue that was dominated by a single isomer, except perhaps the $H_7$CDF, where the 1,2,3,4,6,7,8-isomer would constitute 70% of the homologue. A similar trend was seen with our experimental distributions, and to that extent there was a similarity between experiment and theory. However, with each of the homologues there were important differences between the experimental and theoretical values. In Figure 2, peaks 1 and 2 were significantly lower than predicted by $\Delta G°_{f,600K}$. Other peaks (8−10) were higher in the experiment than predicted by theory. Peak 15, in Figure 3, should be the major component according to theory but was instead quite small. On the other hand, most isomers within $T_4$CDF were predicted to be low, which was the case in the experiment. In Figure 2, peak 43 was too low in the experiment when compared with theory. In Figure 4, peaks 54 and 55 were much lower measured than predicted. Figure 5 had peak 77 as a major component, but it was still lower than predicted

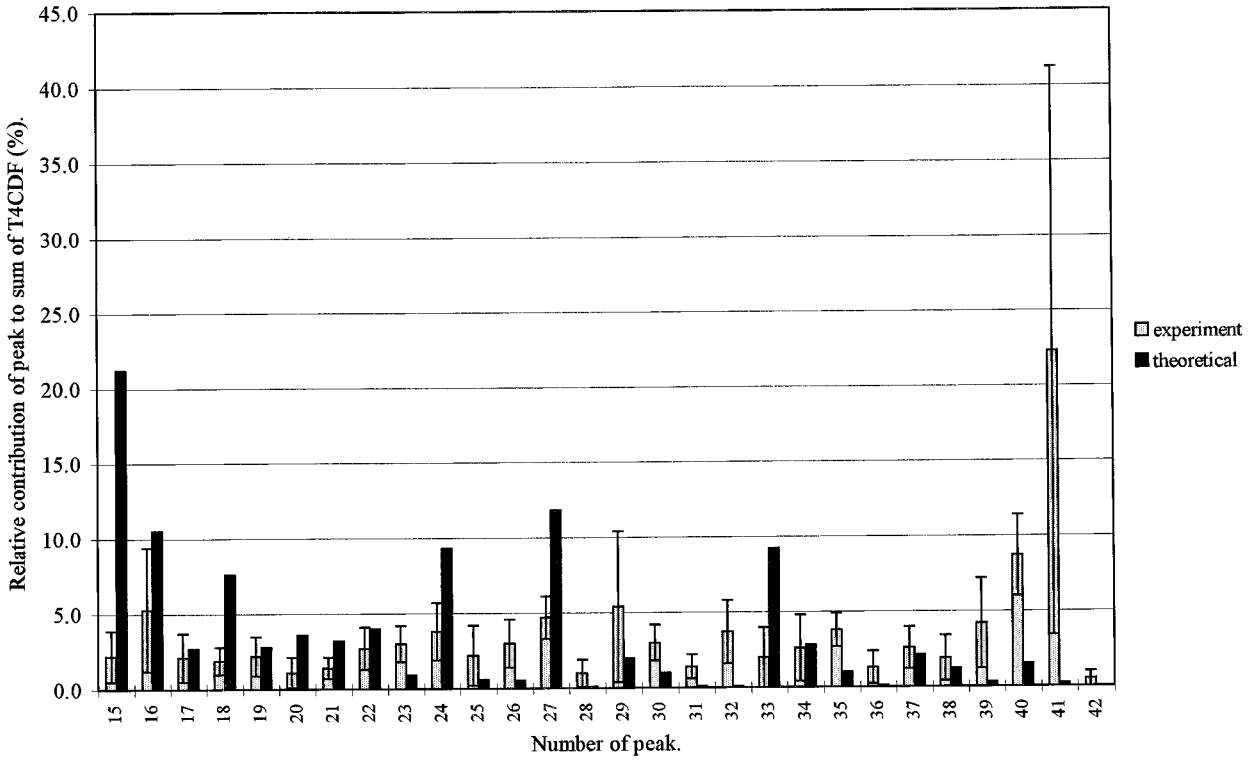


**FIGURE 3. Experimental and theoretical values for $T_4$CDF isomer distribution. Explanation of peak numbers: 15 = 1,3,6,8; 16 = 1,3,7,8 + 1,3,7,9; 17 = 1,3,4,7; 18 = 1,4,6,8; 19 = 1,2,4,7; 20 = 1,3,6,7; 21 = 1,3,4,8; 22 = 1,3,4,6 + 1,2,4,8; 23 = 1,2,4,6; 24 = 1,2,6,8 + 1,2,3,7 + 1,4,7,8; 25 = 1,3,6,9; 26 = 2,3,4,9 + 1,2,3,4; 27 = 1,2,3,8 + 1,4,6,7 + 2,4,6,8 + 1,2,3,6; 28 = 1,3,4,9; 29 = 1,2,7,8; 30 = 1,2,6,7 + 1,2,7,9; 31 = 1,4,6,9; 32 = 1,2,4,9; 33 = 2,3,6,8; 34 = 2,4,6,7; 35 = 1,2,3,9 + 2,3,4,7; 36 = 1,2,6,9; 37 = 2,3,7,8; 38 = 2,3,4,8; 39 = 2,3,4,6; 40 = 2,3,6,7; 41 = 3,4,6,7; 42 = 1,2,8,9.**

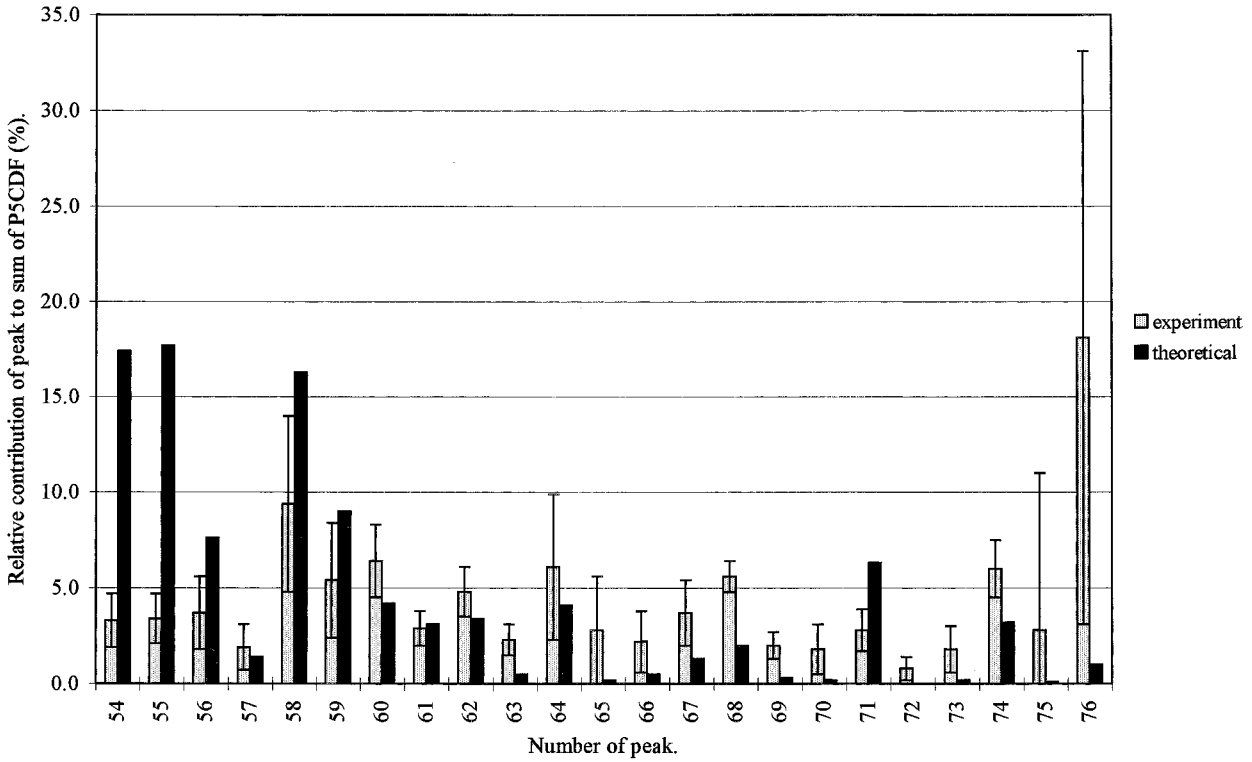


**FIGURE 4. Experimental and theoretical values for $P_5$CDF isomer distribution. Explanation of peak numbers: 54 = 1,3,4,6,8; 55 = 1,2,4,6,8; 56 = 2,3,4,7,9; 57 = 1,3,4,7,9; 58 = 1,3,4,7,8 + 1,2,3,6,8; 59 = 1,2,4,7,8; 60 = 1,3,4,6,7 + 1,2,4,7,9; 61 = 1,2,4,6,7; 62 = 1,2,3,4,7 + 2,3,4,6,9; 63 = 1,3,4,6,9; 64 = 1,2,3,4,8 + 1,2,3,7,8; 65 = 1,2,3,4,6; 66 = 1,2,3,7,9; 67 = 1,2,3,6,7; 68 = 1,2,4,6,9 + 2,3,4,8,9; 69 = 1,3,4,8,9; 70 = 1,2,3,6,9; 71 = 2,3,4,6,8; 72 = 1,2,3,4,9; 73 = 1,2,4,8,9; 74 = 2,3,4,7,8; 75 = 1,2,3,8,9; 76 = 2,3,4,6,7.**

by $\Delta G°_{f,600K}$. Figure 6 showed that peaks 97 and 98 were reversed in formation as compared to theory. However, for the four $H_7$CDF isomers (99−102) there was a remarkable agreement between experiment and theory. From these figures, only this homologue would appear to have a thermodynamically controlled isomer distribution.

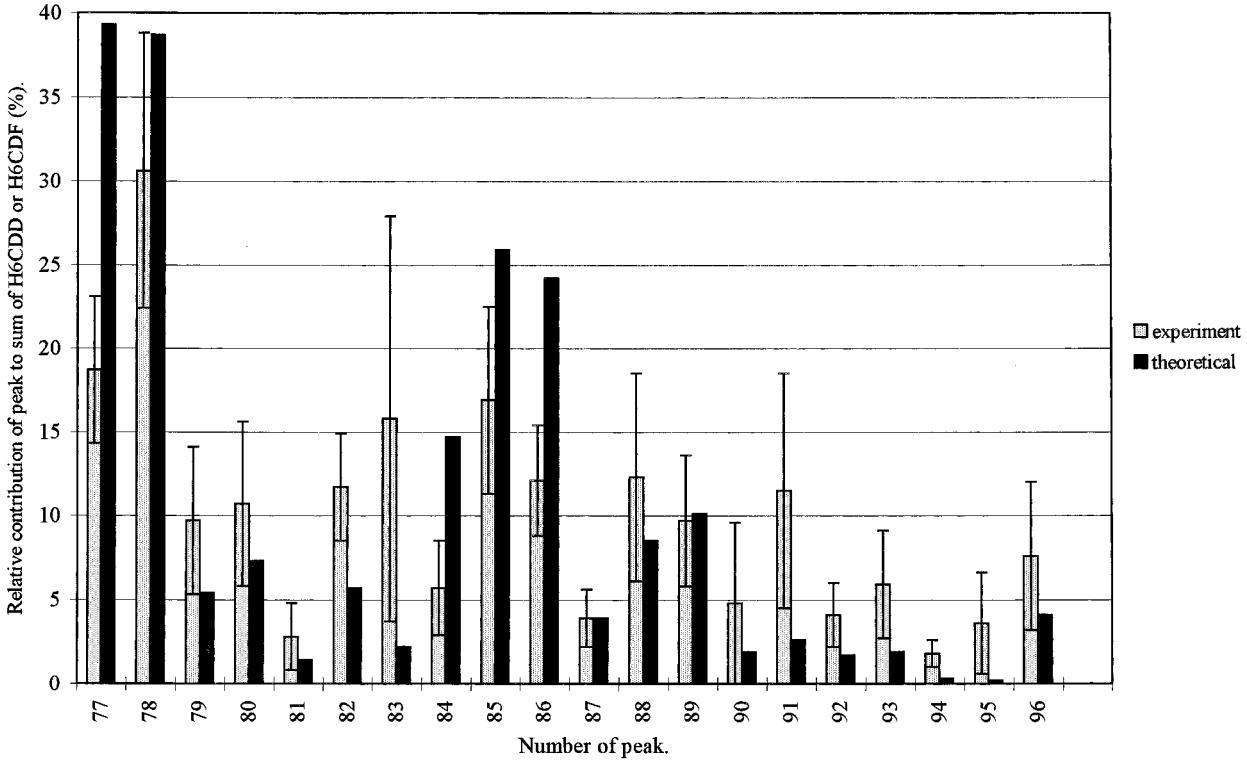


**FIGURE 5. Experimental and theoretical values for $H_6CDD$ and $H_6CDF$ isomer distribution. Explanation of peak numbers: $H_6CDDs$ (peaks 77−83): 77 = 1,2,4,6,7,9 + 1,2,4,6,8,9 + 1,2,3,4,6,8; 78 = 1,2,3,6,7,9 + 1,2,3,6,8,9; 79 = 1,2,3,4,7,8; 80 = 1,2,3,6,7,8; 81 = 1,2,3,4,6,9; 82 = 1,2,3,7,8,9; 83 = 1,2,3,4,6,7. $H_6CDFs$ (peaks 84−96): 84 = 1,2,3,4,6,8; 85 = 1,3,4,6,7,8 + 1,3,4,6,7,9; 86 = 1,2,4,6,7,8; 87 = 1,2,4,6,7,9; 88 = 1,2,3,4,7,8 + 1,2,3,4,7,9; 89 = 1,2,3,6,7,8; 90 = 1,2,4,6,8,9; 91 = 1,2,3,4,6,7; 92 = 1,2,3,6,7,9; 93 = 1,2,3,4,6,9 + 1,2,3,6,8,9; 94 = 1,2,3,7,8,9; 95 = 1,2,3,4,8,9; 96 = 2,3,4,6,7,8.**

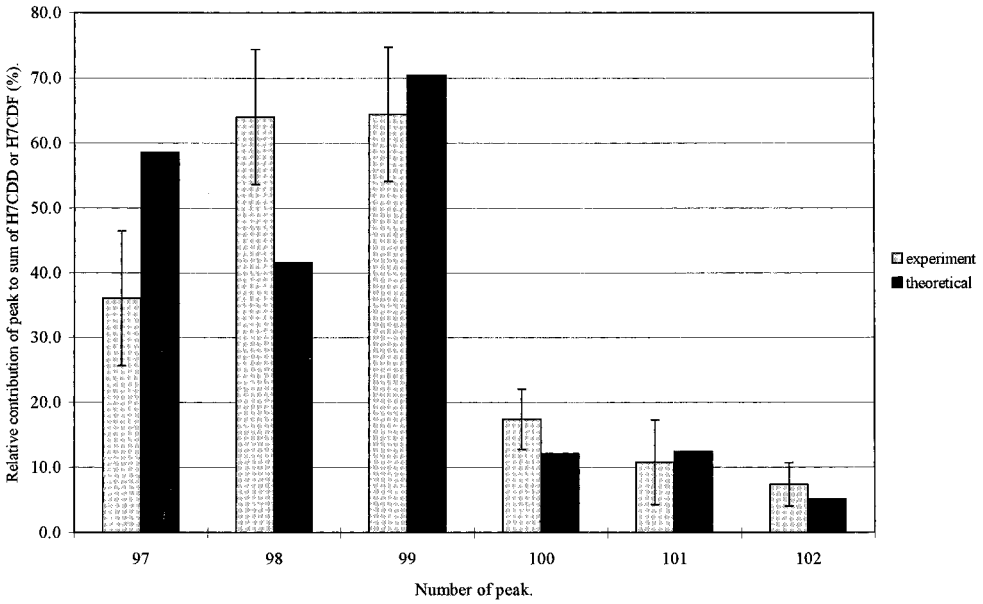


**FIGURE 6. Experimental and theoretical values for $H_7CDD$ and $H_7CDF$ isomer distribution. Explanation of peak numbers: $H_7CDDs$ (peaks 97−98): 97 = 1,2,3,4,6,7,9; 98 = 1,2,3,4,6,7,8. $H_7CDFs$ (peaks 99−102): 99 = 1,2,3,4,6,7,8; 100 = 1,2,3,4,6,7,9; 101 = 1,2,3,4,6,8,9; 102 = 1,2,3,4,7,8,9.**

The results of our investigation showed that the isomer distributions within homologues were independent of the reaction time for de novo formation. This constituted an important argument for thermodynamic control of the chlorination pattern of PCDD/F. Stieglitz et al. reported on a change in isomer distributions as function of time with original fly ash that had not been pretreated and still contained all organics formed on its surface during the incineration (*19*). Since these authors had both carbon and small organic precursors on their fly ash to form PCDD/F, thermodynamically controlled isomer distributions within homologues from carbon could be disturbed by the formation of certain specific isomers from precursors (e.g., from chlorophenols). On the other hand, the lack of isomerization of 1,2,3,4,7,8-$H_6CDD$ on our fly ash suggested that no equilibrium between the various isomers within a homologue existed. Also, the similarity between isomer distributions measured in our experiments and predicted by theory was limited, except for the $H_7CDF$. In summary, there appeared to be arguments both in favor and against thermodynamic

control of isomer distributions within homologues during de novo formation.

As reported in the Introduction, the isomer distributions measured in incinerator effluents appeared to thermodynamically controlled (*4*). This study could not confirm that this was caused by the formation of PCDD/F from carbon, since de novo formation modeled on a laboratory scale yielded arguments both in favor and against thermodynamic control. Further study is needed since thermodynamic properties of PCDD/F could be an easy tool to predict the isomer composition (and hence TEQ value) of a particular sample. Time-based studies with small organic precursors could yield information on changes in isomer distributions under distinctly kinetically controlled conditions. And once the reactant is gone, would the resulting PCDD/F isomer distributions move toward a more thermodynamically favored distribution? Experiments with single PCDD/F congeners could be used to investigate conditions that favor equilibration and isomerization. Further data on $\Delta G^{\circ}_{f,T}$ values of PCDD/F could be used to make a more reliable comparison between experimental and theoretical isomer distributions.

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