

## A Thermodynamic Study on the Isomer Composition of Tetrachlorinated Dibenzo-p-dioxins formed in Combustion Processes

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### 1. Abstract

Three different semiempirical hamiltonians (MNDO, AM1, PM3) are applied for calculations of thermodynamic data for all tetrachlorinated dibenzodioxin isomers. Relative abundances of the isomers are predicted according to the calculated data, assuming an equilibrium between all isomers of the T<sub>4</sub>CDD-homologue under the condition of their formation (thermodynamic controlled dioxin formation mechanism). The computed isomer abundances are compared with those obtained from SHAUB by thermodynamic increment-calculations and with experimental isomer patterns found in combustion samples.

### 2. Introduction

The emission of toxic polychlorinated dibenzodioxins and -furans (PCDD/F) in combustion flue gases (e.g. from waste incinerators or metal works) represents a serious environmental problem (SAFE [1]). In order to develop new strategies for reduction of PCDD/F-emission it is important to learn more about the relevant formation mechanisms. Therefore it is necessary to:

- i) investigate the occurrence of typical PCDD/F isomeric patterns under different, well controlled experimental conditions in model reactions (e.g. WEHRMEIER et al. [2])
- ii) analyze the isomeric patterns of technical combustion processes (looking for *statistical significant* patterns, as performed e.g. by SCHRAMM et al. [3])
- iii) perform more comprehensive theoretical studies on the thermodynamic properties of PCDD and related compounds.

Regarding the third point, isomer-abundances of the tetrachlorinated dibenzo-p-dioxins are calculated by different theoretical approaches (via the *Gibbs Enthalpies of Formation*,  $\Delta G_{\text{T}}$ ), assuming a complete thermodynamic control of PCDD-formation. The computed isomeric equilibrium composition is compared with experimental data from combustion processes (SCHRAMM et al. [3], BACHER et al. [4]).

### 3. Theory

Polychlorinated dibenzo-p-dioxins are formed during combustion processes together with other chloroaromatics on the surface of fly ash-particles in the flue gases at a temperature of about 600 K. This formation process is catalyzed by metal-species (like copper) which occur on the fly-ash surface (see e.g. ADDINK and OLIE [5]). Many researchers found typical isomeric pattern for PCDD formed in combustion processes (e.g. SWEREV and BALLSCHMITER [6], BUSER and RAPPE [7], SCHRAMM et al. [3]). A particular important question is, whether this typical pattern is due to thermodynamically or kinetically controlled formation/destruction reactions during the combustion process. Assuming an equilibrium between all of

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the N isomers of a dioxin homologue (thermodynamic control) at formation conditions (PCDD<sub>1</sub>→PCDD<sub>2</sub> ⇌ ... PCDD<sub>i</sub>...→PCDD<sub>N</sub>) and application of the basic thermodynamic equation:

$$(I) \quad \Delta G_{Tf} = RT \ln K, \quad (K = \text{equilibrium constant})$$

the relative abundance of the PCDD-isomers can be calculated, if the relative *Gibbs Energies of Formation*  $\Delta G_{Tf}$  are known for all isomers. By comparison of the predicted isomer-distributions with those observed in combustion processes, one can confirm or disprove thermodynamic control of the PCDD formation. Recently UNSWORTH and DORANS [8] calculated thermodynamic properties (*Enthalpies of Formation*  $\Delta H_{Tf}$ , *Heat Capacities*  $c_{pT}$  and *Entropies* ( $\Delta S_T$ ) of PCDD and PCDF-isomers for different temperatures by the semiempirical quantum-chemical MNDO method and used this data for PCDD/F-isomer abundance prediction. They concluded, that the comparison of the isomer compositions calculated by MNDO and those observed in wood-soot [4], provides some limited support to the suggestion, that the isomer distribution of individual dioxin homologues may be thermodynamically controlled. However, a recent experimental/theoretical investigation on the ionization potentials of PCDD and chlorinated benzenes by ZIMMERMANN et al. pointed out that the AM1 hamiltonian describes the electronic structure of PCDD more accurate than MNDO [9]. Therefore we reinvestigated the thermodynamic isomer-distribution, using different semiempirical methods (MNDO [10d], AM1 [10c] and PM3 [10e]), in this work. The isomer-distribution obtained by the quantum-chemical calculations as well as those obtained from SHAUBs data [11] (SHAUB used an increment-method, based on thermodynamic properties of model-compounds) are compared with experimental results. The calculations of  $\Delta H_{Tf}$ -,  $\Delta S_T$ - and  $c_{pT}$ -values were performed with the MOPAC quantum chemical program package [10a,b]. Prior to calculation of thermodynamic data for the specified temperatures, the molecular structures were optimized using the respective hamiltonian, by minimizing the calculated *Self Consistent Field* energy ( $E_{SCF} \approx \text{Heat of Formations}$ ) as a function of the atomic positions (BFGS-gradient optimizing routine [10a,b]). The PCDDs exhibit a slightly non-planar molecular structure in the gas phase (e.g. folding angle of ca. 12 ° about the oxygen-oxygen axis for dibenzo-p-dioxin [9b]). In order to achieve correct geometry-optimized structures it was necessary to use input geometries which already exhibit a folded structure, otherwise the BFGS-gradient optimizer converges to a wrong, planar structure as in the case of the calculations from UNSWORTH and DORANS [8] (the planar geometry represents a flat hilltop on the potential-hypersurface and thus the gradient vanishes, pretending geometrical convergence). After the geometry optimization the rotational/vibrational eigenstates were computed (normal coordinate analysis, necessary to determine the contribution of the translational/vibrational/rotational degrees of freedom to the *Entropy* and *Heat Capacity*). Subsequently the thermodynamic data arising from heating the system from 298 K (reference temperature) to the specified temperature were calculated. For calculation of thermodynamic properties, particularly at elevated temperatures, it is important to use correct symmetry numbers [10a], considering the folded geometries of the PCDD (e.g. for 2378-T<sub>4</sub>CDD, point group C<sub>2v</sub>, the correct symmetry number is 2 [9, 10a], not 4 as used in reference [8]). From the MOPAC output data the *relative Gibbs Energies of Formation* are calculated with the most stable congener, chosen as reference compound using equation:

$$(II) \quad \Delta G_{T(598), \text{rel.}} = (\Delta H_{T(598)} - T\Delta S_{(598)}) - (\Delta H_{T(598)\text{ref.}} - T\Delta S_{(598)\text{ref.}})$$

The relative *Gibbs Energies of Formation*  $\Delta G_{T(598), \text{rel.}}$  are calculated from SHAUB's *Heat of Formation- $\Delta H^\circ_{T(298)}$ -values* using the equation

$$(III) \quad \Delta H^\circ_{T(598)} = \Delta H^\circ_{T(298)} + \int_{298}^{598} c_{p(448)} dT$$

as well as the equation (II). The  $c_{p(448)}$  and  $\Delta S_{(598)}$  values are obtained by AM1 calculations ( $c_{p(448)}$  is used due to a linear extrapolation of the temperature dependence of  $c_p$  in the temperature range from 298 to 598 K). Subsequently, the relative abundance of a T<sub>4</sub>CDD-isomer x is given by the equation:

$$(IV) \quad [T\text{CDD}]_x = \{\exp(-\Delta G_{Tf, \text{rel.}}/RT)\} / \left\{ \sum_{i=1}^N \exp(-\Delta G_{Tf, \text{rel.}}/RT) \right\}$$

#### 4. Results and Discussion

In order to estimate the reliability of the different hamiltonians we compared calculated and experimental *Heats of Formation* ( $\Delta H_f^\circ$ ) of polychlorinated benzenes [12,13]. The course of the calculated  $\Delta H_f^\circ$ -values generally fits well with the experimental [12,13] one. However, in accordance with previous reports, which describe problems of the MNDO method to deal with sterically crowded molecules [10b], we observed increasing deviations for higher chlorinated derivatives with MNDO. A comparison of the  $\Delta H_f^\circ$ -predicting power of the MNDO, AM1 and PM3 methods by STEWART [10f] explicitly showed that PM3 and AM1 are more reliable for treating chlorinated compounds than MNDO. This results suggest, that the MNDO method is not superior to the more recent AM1 and PM3 hamiltonians as claimed by UNSWORTH and DORANS [8].

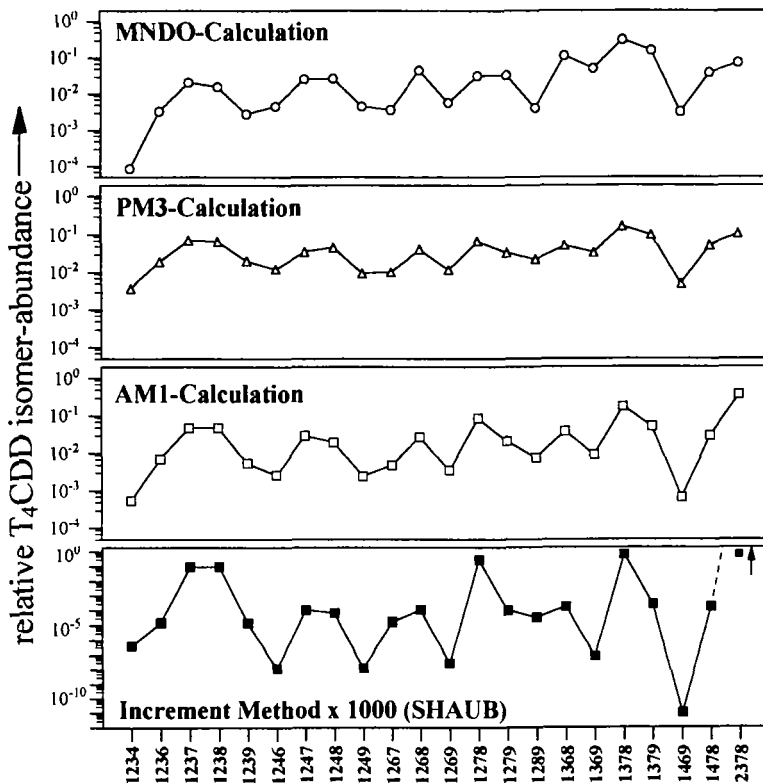


Figure 1  
Relative isomer abundances of the  $T_4$ CDD at 598 K predicted by semiempirical quantum-mechanical methods [10] (MNDO, PM3 and AM1) and by an increment method (SHAUB [11]), assuming a thermodynamic equilibrium during their formation.

However, here we present thermodynamic data and equilibrium compositions of the tetrachlorinated dioxins due to all three methods. The calculated  $\Delta G_{f(598)}^{\text{rel}}$  values and the derived isomer-distributions are listed in table 1. Figure 1 shows the mole fraction of the 22 tetrachlorinated dibenzo-p-dioxin isomers, predicted by quantum chemical MNDO, PM3 and AM1 calculations as well as by SHAUBs increment method at 598 K. The  $\Delta G_{f(598)}^{\text{rel}}$  data obtained from SHAUBs data exhibit the largest variation and the 2378-isomer is predicted to be the most stable one by far. Therefore the isomeric composition based on SHAUBs  $\Delta H_f^\circ$ -values exhibit 99.8 % 2378- and only traces of the other 21  $T_4$ CDDs (which is obviously in contradiction to experimental results). Nevertheless, the relative course of these 21  $T_4$ CDDs compare quite well with those obtained by the quantum-chemical calculations (best correlation to the course of the isomer abundance calculated by AM1). Regarding the totally different approaches on the thermodynamic

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data (quantum chemical calculations and increment method), this coincidence is a good indication for the principal reliability of the quantum chemical methods.

Table 1  
Calculated Gibbs Energy of Formation and relative Abundances for tetrachlorinated dibenzo-p-dioxins. The Gibbs Energy of Formation are given relative to the respective lowest absolute  $\Delta G_{f,598}$  value (i.e. the most stable isomer) as  $\Delta G_{f,598,rel}$ .

T <sub>4</sub> CDD- Isomer	SHAUB-Increments (598 K)		MNDO (598 K)		PM3 (598 K)		AM1 (598 K)	
	$\Delta G_{f,598,rel}$ [kcal/mol]	rel. abund.	$\Delta G_{f,598,rel}$ [kcal/mol]	rel. abund.	$\Delta G_{f,598,rel}$ [kcal/mol]	rel. abund.	$\Delta G_{f,598,rel}$ [kcal/mol]	rel. abund.
1234	25,324	4,00e-10	9,596	8,70e-05	4,416	3,82e-03	7,609	5,56e-04
1236	20,941	1,69e-08	5,315	3,37e-03	2,486	1,99e-02	4,622	7,11e-03
1237	10,74	1,03e-04	3,154	2,14e-02	957	7,33e-02	2,356	4,94e-02
1238	10,721	1,05e-04	3,494	1,60e-02	1,058	6,73e-02	2,357	4,94e-02
1239	21,061	1,53e-08	5,513	2,85e-03	2,432	2,08e-02	4,918	5,52e-03
1246	29,4	1,23e-11	4,938	4,66e-03	3,026	1,25e-02	5,785	2,63e-03
1247	18,722	1,13e-07	2,905	2,65e-02	1,773	3,65e-02	2,942	3,00e-02
1248	19,172	7,67e-08	2,866	2,74e-02	1,479	4,69e-02	3,414	2,00e-02
1249	29,456	1,17e-11	4,945	4,63e-03	3,324	9,71e-03	5,865	2,45e-03
1267	20,812	1,89e-08	5,205	3,71e-03	3,237	1,05e-02	5,042	4,97e-03
1268	18,666	1,18e-07	2,243	4,66e-02	1,615	4,18e-02	3,041	2,75e-02
1269	28,4	2,89e-11	4,666	5,88e-03	3,065	1,21e-02	5,442	3,52e-03
1278	9,508	2,96e-04	2,654	3,28e-02	1,035	6,86e-02	1,685	8,78e-02
1279	18,775	1,08e-07	2,604	3,42e-02	1,831	3,47e-02	3,325	2,16e-02
1289	20,084	3,52e-08	5,067	4,17e-03	2,318	2,29e-02	4,538	7,67e-03
1368	18,114	1,90e-07	1,166	1,17e-01	1,355	5,22e-02	2,626	3,93e-02
1369	27,168	8,28e-11	2,115	5,20e-02	1,828	3,48e-02	4,314	9,26e-03
1378	8,527	6,84e-04	0	3,17e-01	0	1,66e-01	0,859	1,78e-01
1379	17,644	2,83e-07	775	1,63e-01	604	9,91e-02	2,286	5,25e-02
1469	37,693	1,03e-14	5,36	3,25e-03	4,09	5,04e-03	7,414	6,67e-04
1478	18,09	1,93e-07	2,439	3,94e-02	1,331	5,32e-02	2,947	2,99e-02
2378	0	9,99e-01	1696	7,44e-02	502	1,08e-01	0	3,71e-01

The 1378-, 1278-, 1237-, 1238- and partly the 2378-congeners are correspondingly predicted to be the most abundant ones (i.e. congeners with many 2,3,7 or 8 chlorine substituents), whereas the appearance of the 1469-, 1234-, 1246- 1249-, 1269 and 1369-congeners is small (i.e. congeners with no or few 2,3,7 or 8 chlorine substituents). The increased thermodynamic stability of isomers with chlorination in 2,3,7 or 8 position is probably due to the oxygen atom in para position to the chlorine, allowing the formation of (energetically relative favourable) chinoid electronic resonance structures. In figure 2 predicted (with AM1, which is to our conclusion probably the best suited hamiltonian for thermodynamic controlled isomer-abundance prediction) and experimental isomer abundances are compared. The experimental data (table 2) is due to: a) the *first principle component* of a *principle component analysis* (PC-analysis or PCA) obtained from 121 samples, originated mainly from waste incineration (111 from waste incineration, 6 from room fires and 4 from plastic combustion) by SCHRAMM et al. [3]. This data set contains 91% information of the isomer-distribution from the 121 investigated samples and thus represents a good approximation for the "general" T<sub>4</sub>CDD pattern obtained in combustion processes b) the arithmetical mean of 5 samples of waste incineration boiler ash (partly after 2h thermal treatment at 250-400°C). This pattern is mainly due to the *second principal component* observed in the PC-analysis by SCHRAMM et al. [3] and c) a wood burning soot sample, investigated by BACHER et al. [4]. We used only those T<sub>4</sub>CDD-isomers in figure 2 which are resolved in the HRGC-MS measurements. Figure 2 shows, that there is an obvious correlation between the predicted and observed isomer-abundances. The pattern of the tetrachlorinated dioxin-isomers

due to the *principal component analysis* (trace a) is similar to that from the wood soot sample, reported from BACHER et al. (trace c). A strong abundance of the 1368, 1378 and 1379- $T_4$ CDDs, a medium abundance of the 1268 and 2378-isomers and minor abundance of the 1239, 1267, 1269, 1289 and 1478 congeners is observed. However, the pattern of the waste incinerator boiler ash (trace b) exhibit some differences: The relative contribution of the 2378-congener is increased in the latter case, whereas the 1368-isomer abundance is decreased. The isomer pattern of the boiler ash sample (trace b) corresponds to the pattern which is obtained as *second principal component* in the PC-analysis by SCHRAMM et al. [3] and fits very well with the isomer-distribution predicted by the AM1 calculations. The relatively high abundance of the 2378-congener is of particular interest. For the isomeric pattern observed due to the PC-analysis (trace a) and in wood soot (trace c) the coincidence with the AM1 prediction is not as good, but still significant. In conclusion the pattern observed in the boiler ash samples may be due to thermodynamic control in a large extent. The isomer pattern observed in the PC-analysis and in wood soot exhibit a reduced 2378- and an increased 1368- $T_4$ CDD abundance. Therefore at least one elementary reaction within the complex dioxin formation mechanism, may be not controlled by thermodynamics but by kinetics.

Table 2

Relative isomer-abundances for tetrachlorinated dibenzo-p-dioxins observed in combustion processes.

T <sub>4</sub> CDD-Isomer	PCA of 121 Combustion Samples (SCHRAMM et al. [3])	Waste Incinerator Boiler Ash	Wood Burning Soot (BACHER et al. [4]*)
1239	0.0231	0.0192	0.040
1267	0.0160	0.0158	0.022
1268	0.0449	0.0229	0.045
1269	0.0213	0.0194	0.030
1289	0.0169	0.0226	0.038
1368	0.1514	0.0301	0.160
1378	0.1289	0.0921	0.110
1379	0.1367	0.0887	0.100
1478	0.0194	0.0089	0.015
2378	0.0619	0.3992	0.050

\* estimated from their HRGC-MS (SIM) chromatogram in figure No. 1

## 5. Conclusion

The comparison of predicted (thermodynamic reaction control assumed) and experimental isomer patterns of the tetrachlorinated dibenzo-p-dioxins suggest, that thermodynamic control is partly important within the complex dioxin formation mechanism upon combustion processes. On the other hand, there are some obvious deviations between predicted and observed  $T_4$ CDD patterns, indicating that at least one, non thermodynamically controlled mechanism (kinetic control) may be involved additionally. From the environmental point of view it is important, that in the majority of cases the most stable 2378- $T_4$ CDD is not very abundant in the combustion samples ( $T_4$ CDDs with many chlorine substitutions in 2,3,7 and 8 positions are thermodynamically favoured and thus should be prominent in the isomer pattern if total thermodynamic control is assumed). A more detailed knowledge of the dioxin formation mechanism would be important for different reasons. At first, the development of new emission reduction measures would be supported. Further on, one could expect explanations concerning the occurrence of the indicator parameter relation (i.e. the constant relation between PCDD/F and e.g. chlorobenzenes in the stack gas of waste incinerators, see KAUNE et al. [13]). In particular, the indicator parameter approach is of importance for new laser based analytical techniques (e.g. resonance enhanced laser ionization/mass spectrometry, see BOESL et al. [14a] and ZIMMERMANN et al. [14b]) for e.g. on-line emission control. However, in order to get more detailed insights into the molecular mechanism of dioxin formation it is necessary to perform experimental studies (e.g. determination of reaction conditions necessary for generation of the pattern observed in the boiler ash samples). Such studies (WEHRMEIER et al. [2]) are within the field of our current research.

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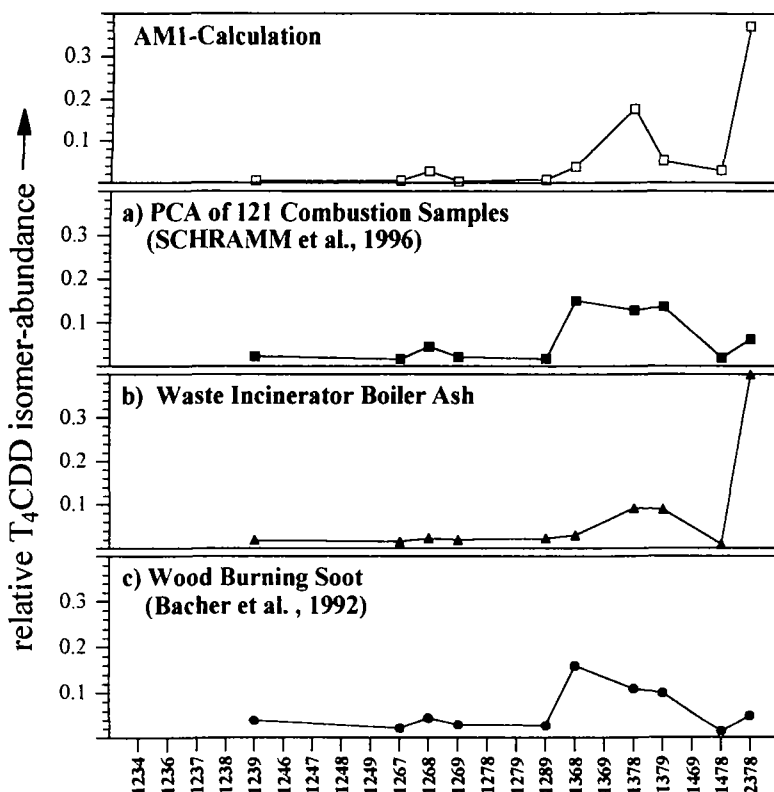


Figure 2  
Comparison of relative isomer abundances of the T<sub>4</sub>CDDs predicted by semiempirical AM1-calculations at a temperature of 598 K and experimental values from PCA (SCHRAMM et al. [3]), waste incinerator boiler ash and wood soot (BACHER et al. [4])

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