CT7 (SL5)   Dioxin Distributions from Combustion: Incinerator Data, Thermodynamic Data, and Kinetic Hypotheses

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Introduction

The formation of dioxin (term used here to refer to both polychlorinated dibenzo-*p*-dioxins, PCDDs, and dibenzofurans, PCDFs) in combustion processes is of concern because of the extreme toxicities of some of these compounds and because of their resistance to degradation in the environment. The number and location of chlorine substituents differentiate dioxin homologues and isomers, respectively. There are a total of 75 PCDD congeners and 135 PCDF congeners. The 17 dioxin congeners with chlorine substituted at all four lateral sites (2,3,7,8) are most toxic; these have been assigned international toxic equivalence factors (ITEQ) ranging from 0.001 to 1. Techniques being developed to measure isomer-specific dioxin emissions in real time can be used to monitor total dioxin emission and total toxic equivalency for health risk assessment if factors controlling dioxin distributions are better understood.

Attempts to correlate **total dioxin** emissions from municipal and hazardous waste incinerators, ranging from 1 to 10,000 ng/dscm, to waste feed parameters, such as chlorine content, as well as to incinerator operating conditions, such as combustion efficiency and gas quench rate, have met with very limited success (Helble, 1993). It has been observed, however, that **dioxin distributions** from combustion exhibit typical features (Fiedler, 1998). Based on the insensitivity of dioxin isomer distributions to combustion conditions, Unsworth and Dorans (1993) proposed that these distributions are thermodynamically controlled. More recently, Wehrmeier *et al.* (1998) found that, while there are similarities between isomer patterns from combustion and thermodynamic stability, there are clear differences as well.

Dioxin are formed in municipal waste incinerators and other combustion processes both at high temperatures in the gas-phase and at low temperatures by fly ash-mediated reactions in air pollution control devices (e.g. electrostatic precipitator). In either case, chlorinated phenols appear to be the primary precursors to dioxin (e.g. Altwicker, 1993). Gas-phase reaction mechanisms have been proposed and refined, most recently by Weber and Hagenmaier (1999); these pathways are illustrated below for 2,3-dichlorophenol. In the radical-molecule route (1), nucleophilic attack by oxygen of the phenoxy radical at a Cl-substituted ortho site of the parent molecule produces an *o*-phenoxyphenol (POP) intermediate with loss of one Cl atom. Subsequent formation of the phenoxyphenoxy radical and ring closure via Smiles rearrangement and the elimination of a second Cl atom yields one of two DiCDD isomers. Dioxin can also be produced by radical-radical mechanisms involving mesomeric structures of the resonance-stabilized phenoxy radical. In route (2), oxygen-carbon coupling of two phenoxy radicals and tautomerization (to regain aromaticity) yields the phenoxyphenol intermediate without loss of chlorine. The second step is the same as that in route (1), this time producing two TriCDD isomers. In route (3), carbon-carbon coupling of phenoxy radicals with two tautomerizations produces a dihydroxybiphenyl (DOHB) intermediate. This sterically demanding coupling does not occur at sites with Cl substitution. Subsequent H₂O elimination produces a TetraCDF. Thus, PCDD formation requires at least one of the phenol precursors to have an ortho chlorine substituent whereas PCDF formation requires each of the precursors to have at least one unsubstituted ortho site. When both ortho sites of the phenol are unsubstituted, three carbon-carbon couplings are possible, resulting in the formation of three PCDF isomers.
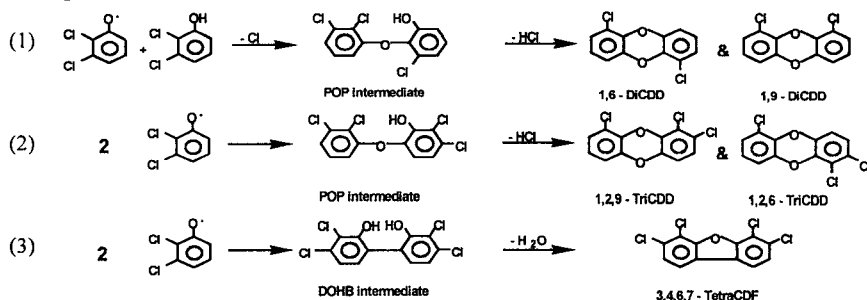
In this paper, typical features in dioxin isomer distributions from municipal waste incinerators are enumerated. These combustion distributions are then compared with calculated thermodynamic isomer distributions. Results of laboratory experiments are used to identify thermodynamic and kinetic factors controlling isomer distributions from single chlorinated phenol precursors. Finally, hypotheses concerning kinetic effects when a distribution of phenol precursors is present are proposed.

Municipal Waste Incinerator Distributions

In 1988, extensive field tests were conducted at the Montgomery County municipal waste combustion facility in Dayton, Ohio, to study effects of incinerator parameters on dioxin formation (von Alten et al., 1992). Total tetra through octa homologue concentrations as well as 2,3,7,8 congeners were measured in gas streams sampled at the outlet of the rotary kiln combustor and at the inlet and outlet of the electrostatic precipitator (ESP). Negligible dioxin concentrations were detected at the ESP inlet, indicating that essentially all of the dioxin formed in the kiln were removed from the exhaust gas in the conditioning chamber prior to the ESP. Thus, data from the kiln outlet and the ESP outlet (stack) provide a measure of dioxin formed at high and low temperatures, respectively. Six tests were conducted to study effects of ESP temperature, kiln temperature, and limestone injection.

Measurements of PCDF-to-PCDD mass ratio (PCDF/PCDD), homologue distributions (tetra through octa), and 2,3,7,8 isomer fractions are listed in Table 1. While total dioxin ranged from 57 to 15,800 ng/dscm, increasing with increasing ESP temperature and decreasing with limestone injection, these distributions did not vary significantly in the six tests. Based on these data, as well as other published municipal waste incinerator data for which homologue patterns were measured in both the combustor and stack (O'Keefe et al., 1989; Tanaka et al., 1989; Benfenati et al., 1991), three observations are made: (1) PCDF formation is favored at high temperatures (kiln); (2) chlorination is less at high temperatures; (3) PCDDs are more chlorinated than PCDFs. These observations are consistent with PCDDs being less stable than PCDFs, organic chlorine being less stable at high temperatures, and increased chlorination favoring nucleophilic attack and, therefore, PCDD formation. The typical homologue profile shown in Table 1 (Fiedler,1998) is most like the stack profile for PCDDs and the kiln profile for PCDFs, consistent with PCDDs formed mostly at low temperatures and PCDFs favored at high temperatures.

The 2,3,7,8 isomer fractions measured at the Montgomery County incinerator are largely unaffected by changes in incinerator operating conditions. Moreover, these fractions are similar to those measured in incinerator ash samples in Japan (Yasuhara et al., 1987), The Netherlands (Addink et al., 1991) and Germany (Wunsch et al., 1994). At all of these incinerators, 2,3,7,8 isomer fractions are greater than that statistically predicted, based on the number and symmetry of isomers in the homologue, with three exceptions: 1,2,3,4,7,8-HxCDD, 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF. These three 2,3,7,8 dioxin that are not favored relative to statistical abundances each have structural features associated with high steric hindrance. 1,2,3,4,7,8-HxCDD has a fully chlorinated ring. 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF have both bay sites occupied by chlorine atoms. Thus, steric factors appear to be important determinants of dioxin isomer distributions.

Table 1. Dioxin distributions from the Montgomery County municipal waste incinerator.

PCDF/PCDD (mass): 3.8"1.0 (kiln); 0.8"0.2 (stack); 2 (typical[a])

homologue	Kiln	stack	typical[a]	homologue	kiln	stack	typical[a]
TeCDD	12.6"3.5	1.6"1.8	7	TeCDF	40.0"8.3	9.1"6.3	30
PeCDD	18.1"4.1	5.6"3.8	13	PeCDF	29.5"5.3	11.3"4.8	37
HxCDD	25.4"2.7	18.8"9.5	16	HxCDF	18.2"3.2	19.5"8.5	23
HpCDD	29.9"5.4	36.8"6.0	32	HpCDF	8.1"2.2	34.2"6.0	8
OCDD	14.0"3.6	37.3"13.	32	OCDF	4.1"4.7	26.0"10.	2

PCDD isomer	kiln	stack	statistical[b]	PCDF isomer	kiln	stack	statistical[b]
2378-	8.2"1.8	6.9"2.9	1.4	2378-	3.8"0.5	3.3"1.5	1.4
12378-	14.6"1.5	10.7"3.6	7.1	12378-	8.0"2.1	4.5"1.3	3.6
123478-	4.8"1.2	3.9"0.8	7.1	23478-	8.1"2.9	14.7"2.4	3.6
123678-	10.4"1.6	12.1"0.4	7.1	123478-	15.0"1.7	18.0"3.6	7.1
123789-	19.3"0.5	16.2"3.0	7.1	123678-	12.0"1.9	9.7"1.9	7.1
1234678-	54.5"2.5	54.0"3.0	50	234678-	12.7"2.9	32.3"9.8	3.6
				123789-	1.3"0.6	1.1"1.0	3.6
				1234678-	42.5"2.8	45.3"13.	25
				1234789-	14.3"2.5	10.8"3.1	25

[a] Typical municipal solid waste incinerator emissions (Fiedler, 1998).
[b] Statistical percentage based on number of isomers in homologue and symmetry.

Correlation of Combustion and Thermodynamic Isomer Distributions

Qualitative observations regarding the effect of steric hindrance on the distribution of dioxin isomers in incinerator emissions can be assessed quantitatively by computational molecular modeling. Thermodynamic isomer distributions of dioxin are governed by statistical factors and steric effects associated with features of molecular structure. While measured thermodynamic data for dioxin are not available, dioxin properties have been estimated by group additivity and semiempirical and *ab initio* molecular orbital modeling methods. Additivity groups have not been derived for property differences of complete sets of dioxin isomers. The computational requirement for *ab initio* calculations to obtain the degree of accuracy necessary to differentiate all dioxin isomers is still quite large. Therefore, we used three semiempirical methods, MNDO, AM1 and PM3, to estimate standard enthalpies, ΔH^0, and entropies, S^0, as a function of temperature for all 75 PCDD congeners and 135 PCDF congeners. The AM1 and PM3 methods yield the same order of stability, based on heats of formation, for dioxin isomers; minor differences in this ranking were found using the MNDO method due to its overestimation of steric hindrance associated with vicinal chlorine substitution. AM1 and PM3 results are presented here. For PCDDs, chlorine substitution at lateral sites (2,3,7,8) is more stable than at ortho sites (1,4,6,9). For PCDFs, chlorine substitution at lateral sites (2,3,7,8) is most stable, then one bay site (1,9), then ortho sites (4,6), and lastly both bay sites. For example, dichlorinated dioxin isomers have the following order of stability:

PCDDs: 2,7~2,8 > 2,3 > 1,7~1,8 > 1,3 > 1,2 > 1,6 > 1,9 > 1,4

PCDFs: 2,8~2,7~3,7 > 1,8~1,7 > 1,3 > 2,3 > 2,6~3,6 > 1,2 > 2,4 > 1,6 > 1,4 > 3,4 > 4,6 > 1,9

Thermodynamic isomer distributions were calculated as follows:

$$X_i(T) = 1/\{1+3\exp(-\Delta G^0_{ji}(T)/RT)\}$$

Here, X_i is the mole fraction of isomer i at temperature T, N is the total number of isomers in a homologue, and ΔG^0_{ji} is the difference in the total Gibbs free energy between isomers j and i. In Figure 1, PM3 thermodynamic isomer distributions are compared with a complete set of tetra through octa congeners measured at a German municipal waste incinerator (Wunsch *et al.*, 1994). Data are plotted as the logarithm of the ratio of measured or thermodynamic isomer fraction to statistical isomer fraction; therefore, the deviation from zero indicates the deviation from a statistical fraction. The positive correlations in Figure 1 indicates the degree to which a deviation from a statistical distribution can be predicted by thermodynamic differences between isomers, which are largely due to steric effects. For both PCDDs and PCDFs, the PM3 results are most correlated with the incinerator distributions and the MNDO results are least. By all three methods, incinerator isomer distributions are more correlated with thermodynamic distributions for PCDDs than for PCDFs.

Also identified in Figure 1 are congeners that are found in much higher amounts in incinerator emissions than predicted thermodynamically. For PCDDs, these are congeners with a meta substitution pattern: 1,3,6,8- and 1,3,7,9-TetraCDDs. For PCDFs, these are congeners with Cl substituents at the 3,4,6,7 positions (3,4,6,7-TetraCDF, 2,3,4,6,7-PentaCDF, and 1,2,3,4,6,7- and 2,3,4,6,7,8-HexaCDFs) as well as at the 1,9 positions (e.g. 1,4,6,9-TetraCDF). While inaccuracies in the thermodynamic distributions estimated using the semiempirical methods might explain some of the differences between measured and thermodynamic isomer fractions, kinetic effects are likely responsible for most of the differences, as explained next.
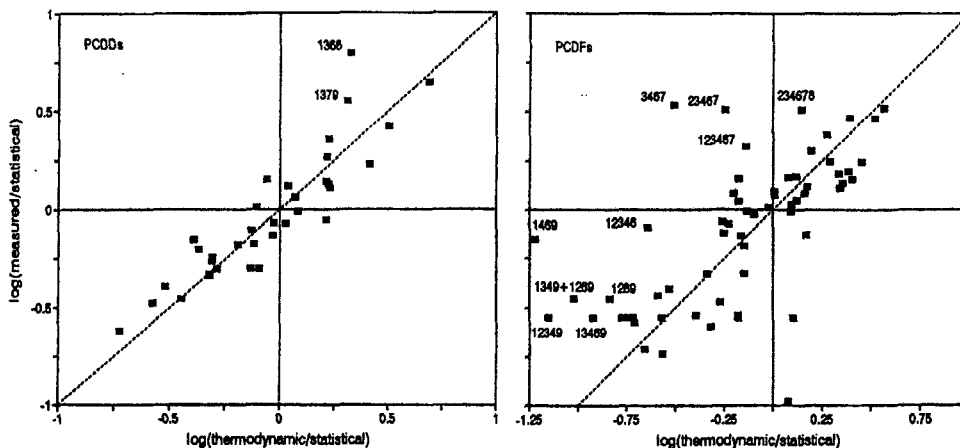

Figure 1. Isomer distributions from a municipal waste incinerator (Wunsch *et al.*, 1994) and PM3 thermodynamics.

Laboratory Experiments and Kinetic Hypotheses

The temperature dependent formation of 1,6- and 1,9-DiCDD isomers from 2,6-dichlorophenol and 1,7-,3,7- and 1,9-DiCDF isomers from 3-chlorophenol was studied experimentally in an isothermal flow reactor over the range 300 to 900°C under pyrolytic, oxidative and catalytic conditions. Measured and calculated thermodynamic isomer fractions are shown in Figure 2. At high temperatures, dioxin product isomer fractions are consistent with thermodynamic calculations. At low temperatures, however, this is not the case. For 1,6- and 1,9-DiCDD formed from 2,6-dichlorophenol, the 1,6 isomer fraction is greater than that thermodynamically predicted at low temperatures. We postulate that six-membered ring closure of the POP intermediate which produces only 1,6-DiCDD competes with the five-membered ring Smiles pathway which produces both isomers. AM1 transition state calculations indicate the six-membered ring closure pathway has a lower activation energy by 3.9 kcal/mol than the Smiles rearrangement pathway, which is consistent with the experimental results (dashed curves). For 1,7-, 3,7- and 1,9-DiCDF formed from 3-chlorophenol, the 1,7 isomer fraction exceeds thermodynamic prediction at low temperatures. This result can be attributed to steric effects in alternative Asandwich-type@ approach geometries of phenoxy radicals to form the DOHB intermediate (Armstrong et al., 1983); this is currently being studied computationally.
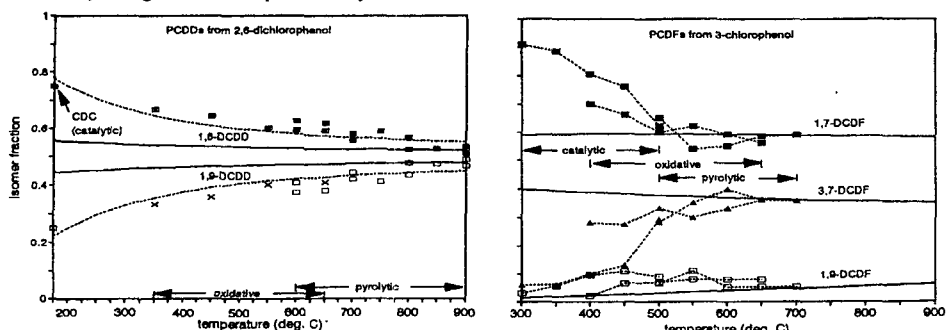

Figure 2. Isomer distributions from laboratory experiments and AM1 computations (Mulholland et al., 1999).

Thus, for affine reactions that produce dioxin in combustion systems, it is not surprising that thermodynamic properties are correlated with kinetic rates. Differences in combustion and thermodynamic isomer patterns can be used to elucidate mechanism. In addition to the kinetic effects discussed above for dioxin formed from single precursors, there are effects due to the distribution and relative reactivities of different phenol precursors. The most abundant chlorinated phenols found in combustion gas are the 2,4,6 congeners. 2,4,6-Trichlorophenol produces 1,3,6,8- and 1,3,7,9-TetraCDD, the two PCDD congeners found in significantly greater concentrations in combustion samples than thermodynamically predicted. Laboratory experiments suggest that, while ortho/para Cl substitution of phenols promotes PCDD formation, meta substitution favors PCDF formation. For example, 2,3-dichlorophenol, which has one ortho Cl and one ortho H, yields 3,4,6,7-TetraCDF predominantly. Phenols with Cl at both meta sites produce PCDFs with 1,9 Cl substituents. Such kinetic effects may explain the high concentrations of these PCDFs found in combustion samples.

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