

FORMATION AND SOURCES II

SOME KINETIC ASPECTS ON THE FORMATION OF TYPICAL QUASI-STATIONARY PCDD/PCDF MIXTURE IN THERMAL SOURCES

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Introduction

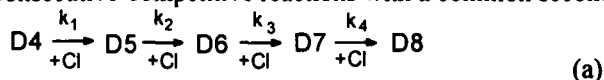
It has been earlier reported that a typical mixture of isomers from tetra- to heptachlorodibenzo-*p*-dioxins and dibenzofurans is formed in the combustion processes¹. To explain it there has been a suggestion made that the electronic factors may have a substantial impact on the chlorination pathway².

In this work, there is an attempt performed to assess the ratio of rate constants for the chlorination of 2,3,7,8-tetrachloro derivatives of dibenzo-*p*-dioxins and dibenzofurans (17 toxic congeners, Table 1), which occurs in thermal sources.

Methods and Materials

Since waste incinerators could be considered as the open systems of "ideal mixing" type, the order of magnitude for the chlorination rate constants can be estimated³. The use of "ideal displacement" approach requires another calculation technique, but the results do not differ.

The chlorination of 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (-DD) and 2,3,7,8-tetrachloro-dibenzofuran (-DF) is an example of well-known consecutive-competitive reactions with a common second reagent.



The rate of chlorination R_i for each of congeners is directly dependent on the concentration of active chlorine in the gaseous mixture and equals:

$$R_i = \text{const} \cdot k_i \cdot C_{Cl} \quad (b)$$

where k_i is the rate constant, and C_{Cl} is the overall concentration of active chlorine. The system of algebraic expressions for (a) can be written as follows:

$$-k_1 C_{D4} + \alpha C_{D4}^0 - \alpha C_{D4} = 0 \quad (1)$$

$$k_1 C_{D4} - k_2 C_{D5} - \alpha C_{D5} = 0 \quad (2)$$

$$k_2 C_{D5} - k_3 C_{D6} - \alpha C_{D6} = 0 \quad (3)$$

$$k_3 C_{D6} - k_4 C_{D7} - \alpha C_{D7} = 0 \quad (4)$$

$$k_4 C_{D7} - \alpha C_{D8} = 0 \quad (5)$$

Here C_i is the concentration of *i*-congener, C_{D6} is the sum of 2,3,7,8-substituted congeners of hexachloro-DD, $\alpha = v/V$ where v is the flux rate of reactive gases and V is the reactor volume, and C_{D4}^0 is the initial concentration of 2,3,7,8-tetrachloro-DD. The active chlorine concentration is assumed constant and high and is not included into calculations on this stage. It follows from (5) that

$$k_4 = \alpha C_{D8} / C_{D7} \quad (6)$$

Substituting this expression into (4) we obtain:

$$k_3 = \alpha (C_{D8} + C_{D7}) / C_{D6} \quad (7)$$

FORMATION AND SOURCES II

Following the same pattern, from (3) and (2) we can derive:

$$k_2 = \alpha (C_{D8} + C_{D7} + C_{D6}) / C_{D5}, \quad (8)$$

$$k_1 = \alpha (C_{D8} + C_{D7} + C_{D6} + C_{D5}) / C_{D4}. \quad (9)$$

As a result of substitution of the last expression into (1) we obtain the following:

$$\alpha (C_{D4}^0 - C_{D4} - C_{D5} - C_{D6} - C_{D7} - C_{D8}) = 0$$

Since $\alpha = 0$, then $C_{D4}^0 = C_{D4} + C_{D5} + C_{D6} + C_{D7} + C_{D8}$. The analogous procedure has been performed for dibenzofurans (DF).

Results and Discussion

2,3,7,8-TCDD/F - initial components. The existence of a typical quasi-stationary mixture of 17 toxic congeners is explained by the prevailing pathway of their formation via the electrophilic chlorination mechanism (ECM) for 2,3,7,8-TCDD and 2,3,7,8-TCDF. This mechanism favors the *ortho*-orientation of chlorine to oxygen atoms⁴. The authors of⁵ has come to the same conclusion. The observed *para*-orientation, which is also typical for ECM is one-two order in magnitude weaker. It could be supposed that *ortho*-orientation is typical for the kinetic control of the reaction, while *para*-orientation reflects the thermodynamic stability due to the resonance with chinoid structure⁶.

The authors suggest that to explain the content of congeners it necessary to consider at least one pathway, which is not controlled by thermodynamics (kinetic control).

The use of ECM approach with respect to the chlorination of non-chlorinated dioxins and furans (DD and DF) shows that kinetic control according to the *ortho*-substitution mechanism should preferably give 1,4,6,9-tetrachlorosubstituted DD, though the content of the investigated mixtures disprove this conclusion. The 1,4,6,9-TCDD congener, which should dominate according to ECM is present in the mixture in minor concentrations. Therefore, the contribution of the pathway, which accounts for the formation of the congeners mixture via the chlorination of non-chlorinated DD and DF is neglectfully small. The question of the contribution of other pathways (chlorophenol

Table 1

| No. | Name | Compound |
|-----|------|------------------------|
| 1 | D4 | 2,3,7,8-TetraCDD |
| 2 | D5 | 1,2,3,7,8-PentaCDD |
| 3 | D61 | 1,2,3,4,7,8-HexaCDD |
| 4 | D62 | 1,2,3,6,7,8-HexaCDD |
| 5 | D63 | 1,2,3,7,8,9-HexaCDD |
| 6 | D7 | 1,2,3,4,6,7,8-HeptaCDD |
| 7 | D8 | OctaCDD |
| 8 | F4 | 2,3,7,8-TetraCDF |
| 9 | F51 | 1,2,3,7,8-PentaCDF |
| 10 | F52 | 2,3,4,7,8-PentaCDF |
| 11 | F61 | 1,2,3,4,7,8-HexaCDF |
| 12 | F62 | 1,2,3,6,7,8-HexaCDF |
| 13 | F63 | 1,2,3,7,8,9-HexaCDF |
| 14 | F64 | 2,3,4,6,7,8-HexaCDF |
| 15 | F71 | 1,2,3,4,6,7,8-HeptaCDF |
| 16 | F72 | 1,2,3,4,7,8,9-HeptaCDF |
| 17 | F8 | OctaCDF |

and chlorobenzene condensation, aromatization of chlorinated acetylenes and carbon particles, and PCB oxidation) into the content of quasi-stationary mixture of 17 toxic congeners has been discussed in many works.^{5,7} Nevertheless, it can be concluded that the complete chlorination (up to octachloro-DD/DF) of 2,3,7,8-TCDD/DF, which have been pre-formed by the different mechanisms provides the major contribution. Therefore, the typical distribution of 17 toxic congeners is due to that 2,3,7,8-TCDD/DF is the initial component and the chlorination follows according to ECM.

Role of chlorine. It is commonly assumed that the active form of chlorine in gaseous reactions is the Cl[•] radical, which is formed by the decomposition of chlorine molecule. Nevertheless, the polarized HCl or the covalently bound organic chlorine might be the active part as well⁸. The same is true for the

FORMATION AND SOURCES II

inorganic salts of the Me^+Cl^- type^{9,10}. It is not critical for the kinetic analysis performed here. It is important to know that the concentration of active chlorine in the stationary (by content, temperature, and rate) flux of reacting gases would also stay constant. The overall rate for the PCDD/DF formation and for each congener in particular would be directly dependent on the concentration of active chlorine. The active particle attacks each of the subsequent chlorination products (D5, D6 congeners, etc.) not depending on the concentration of others. Therefore, the ratio of the observed rate constants would conform to the ratios of the rate constants for the particular elementary steps not depending on the kinetic equations. In the framework of a particular process the assumption on the constancy of chlorine concentration is sound though the possible variations could have a strong impact on the chlorination rate by accelerating or suppressing it hundreds or thousands times (see Table 2). These variations would not have any influence on the reaction mechanism that is confirmed by the analysis of slopes on the plots "congener concentration vs. congener No. from Table 1". These plots show that the concentration ratios pointed above stay the same for each source of emission. Therefore, the concentrations (yields) of all congeners are directly linked to the chlorine concentration in gases. It is in the full accordance with the data^{11,12}.

Process parameters. The data on the process parameters of incinerators are rather scanty. To estimate the parameter we may use the characteristics of the plant in Vienna¹³. This plant incinerates 40 tons of waste per hour forming 0.97 tons/hr of fly ash, which contain copper (chlorination catalyst) in 890 mg/kg amount and emitting 230 tons/hr of gases. Starting from these data and taking that the gas density corresponds to that of nitrogen (MW 28 and 18% vol. content in gaseous mixture) we obtain the gaseous flux of $200 \cdot 10^3 \text{ m}^3/\text{hr}$, or nearly $50 \text{ m}^3/\text{sec}$.

We have two possibilities to estimate the volume value (V):

1) We may assume that the volume of the reacting gaseous mixture corresponds to the "two seconds rule", i.e. the gas stays at high temperature no shorter than 2 seconds. Then our "reactor" would have the volume of $V = v \cdot 2 \text{ s}$. Since $v = 50 \text{ m}^3/\text{s}$, then $V = 100 \text{ m}^3$. In this case, $\alpha = v/V$ will always be equal to 0.5 s^{-1} not depending on the gas flux that is very convenient for calculations.

2) Nevertheless, it is assumed that chlorination proceeds on the surface of fly ash in the presence of a catalyst. Then, the "reactor" volume would be equal to the volume of fly ash per time unit. We also assume that the surface of fly ash is continuously renewed. If we assume that its density is close to 1, then with its formation rate of $1 \text{ m}^3/\text{hr}$ the volume per second is $V = 0.0003 \text{ m}^3$ (3 cm^3) and $\alpha \cong 1.7 \cdot 10^5 \text{ s}^{-1}$. Therefore, these two calculation approaches differ by 6 order of magnitude and it is necessary to apply some other assumptions to choose between them.

Observed (calculated) chlorination rate coefficient. To assess the magnitudes of the chlorination rate constants we took the data on two French (A and B)¹⁴ and one Russian municipal solid waste incinerators (MSWI)¹⁵. MSWI-A: 4 runs, MSWI-B: 2 runs, and Moscow MSWI: one run. The results are reported in Table 2.

It is clearly seen that all the constants are in agreement for plant A and the deviation from the mean value is no more than 2-30%. At the same time the data on plant B strongly differ from each other and from the data on plant A. It may result from instability in the work of incinerator B.

Narrow data distribution for incinerators A and B allows to conclude that α value is quite stable for each incinerator at the constant inlet of waste. The productivity and other properties of Moscow plant differ from French incinerators significantly that reflects in the constants obtained.

FORMATION AND SOURCES II

Table 2

| | Rate constants* | MSWI-A | | | | MSWI-B | | Moscow MSWI |
|------|-----------------|---------|---------|---------|---------|---------|----------|-------------|
| | | 1 | 2 | 3 | 4 | 1 | 2 | |
| PCDD | k ₁ | 47618.8 | 40274.3 | 68385.3 | 53448.1 | 23978.4 | 838068.7 | 130.96 |
| | k ₂ | 7194.7 | 6327.3 | 10626.7 | 9117.4 | 2478.8 | 23386.9 | 33.22 |
| | k ₃ | 386.3 | 484.6 | 676.9 | 589.6 | 111.8 | 453.8 | 7.35 |
| | k ₄ | 15.9 | 22.3 | 24.6 | 19.9 | 7.25 | 19.5 | 3.99 |
| PCDF | k ₁ | 557.0 | 552.1 | 1452.7 | 786.9 | 331.2 | 44600.9 | 2.31 |
| | k ₂ | 194.7 | 173.3 | 417.0 | 240.9 | 110.8 | 390.5 | 3.49 |
| | k ₃ | 69.3 | 71.4 | 125.9 | 98.6 | 33.6 | 112.3 | 1.17 |
| | k ₄ | 5.65 | 5.1 | 7.8 | 6.9 | 2.95 | 7.99 | 0.92 |

*) Rate constant does not include α parameter and chlorine concentration and can be only used for comparison.

At the same time the comparison of the observed rate constants for the chlorination of toxic congeners for all the considered incinerators shows that the chlorination rate suddenly drops from tetra- to heptachlorinated congeners. It is probably connected with the passivating effect of chlorine in the electrophilic aromatic substitution. The chlorination rate distribution within the isomer groups is also connected with ECM, *i.e.* with the prevailing of *ortho*-substitution^{2,4} though it requires special kinetic analysis.

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