Kinetics and Mechanism of Thermal Degradation of Octachloro-dibenzofuran and Octachlorodibenzo-p-dioxin Spiked on Fly Ash.

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1. Introduction

The presence of PolyChlorinated Dibenzo-p-Dioxins (PCDD) and PolyChlorinated DibenzoFurans (PCDF) in Municipal Solid Waste (MSW) incinerator effluents is a well-established fact [1]. It has been shown [2] that homogeneous gas-phase reactions cannot be the sole source of PCDD/F level in MSW incinerator effluents. Today, there is evidence that fly ash promotes the postfurnace formation of these compounds in MSW incinerators, resulting in fly ash and gas stack PCDD/F levels that by far exceed those measured at the furnace exit.

In recent years a variety of investigations on the formation and degradation mechanisms have been performed for better insight of the gas-phase and heterogeneous reactions at the relatively low temperatures typical of boiler sections and electrostatic precipitators. However, the degradation kinetics and mechanism have not been so intensively investigated as those of formation. Thermal degradation has been studied on different scale basis under different conditions. In these studies, only the octa- to tetra-chlorinated PCDD\PCDF were analyzed as possible degradation products. As the mass balance is never satisfied, it was postulated that two reaction pathways, dechlorination and decomposition, operate simultaneously [3].

The aim of our research is to establish the relative importance of the two pathways and to identify the degradation mechanisms. As little is known about energies involved in chemical reactions on fly ash, the determination of kinetic constants and activation parameters is necessary. Here the degradation kinetics of Octachlorodibenzofuran (OCDF) and Octachlorodibenzo-p-dioxin (OCDD), both spiked on fly ash are reported; the first being studied in nitrogen stream and the second in air stream.

2. Experimental

Fly ash from a waste incineration plant was spiked with OCDF or OCDD. Degradation of OCDF/OCDD occurs by thermal treatment of the fly ash in nitrogen or air in presence of water vaporous. The following reaction parameters were varied: temperature, time, presence/absence of water vapour. The reaction temperatures were chosen ranging between 200°C and 350°C, the reaction time ranging between 15 and 240 minutes.

Reaction products were identified and quantified by GC-MS analysis.

The experimental and analytical procedures are described elsewere [4] and are not reported here.

3. Kinetic scheme

The experimental data for OCDF and OCDD for the various runs are not reported here.

To interpret the reagent behavior, the following kinetic scheme is proposed.

First a partition between "free" or "slightly", physically adsorbed reactant molecules, R_f, and "strongly", chemically adsorbed molecules, R_a, was postulated.

The physically adsorbed reagent was identified with the species which undergo the decomposition reaction whilst the chemiadsorbed reagent was identified with those which undergo the dechlorination reaction. The former reaction is probably not catalyzed and the latter is. The following kinetic reaction scheme is hypothesized:

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■ *Partition constant*:

$$K = \{1/[OCDF_f]_0\} \, [OCDF_a]_0/\{[OCDF]_0 - [OCDF_a]_0\}$$

■ *Decomposition reaction*:

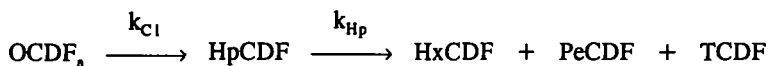$$OCDF_f \xrightarrow{\;k_D\;} P_D$$
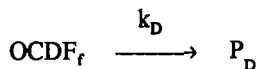
$$d[OCDF_f]/dt = - k_D \, [OCDF_f]$$

$$[OCDF_f]/[OCDF_f]_0 = \exp(- k_D t)$$

and

$$C_D/[OCDF]_0 = [OCDF_f]_0/[OCDF]_0 \, [1 - \exp(- k_D t)]$$

■ *Dechlorination reaction*:

$$OCDF_a \xrightarrow{\;k_{Cl}\;} HpCDF \xrightarrow{\;k_{Hp}\;} HxCDF + PeCDF + TCDF$$

$$d[OCDF_a]/dt = - k_{Cl} \, [OCDF_a]$$

$$[OCDF_a]/[OCDF_a]_0 = \exp(- k_{Cl} t)$$

and

$$d[HpCDF]/dt = k_{Cl} \, [OCDF_a] - k_{Hp} \, [HpCDF]$$

$$[HpCDF]/[OCDF]_0 = [HpCDF]_0/[OCDF]_0 \, \exp(- k_{Hp} t) +$$

$$[OCDF_a]_0/[OCDF]_0 \, [k_{Cl}/(k_{Hp} - k_{Cl})] \, [\exp(- k_{Cl} t) - \exp(- k_{Hp} t)]$$

3. Results

The OCDF and OCDD data were fitted with two different mathematical procedures [4].
Table 1 reports the first-order kinetic constants calculated for the disappearance of OCDD and OCDF. Tables 2 and 3 report the calculated values of C_{Rf}/C_R^0, k_D, C_{Ra}/C_R^0, k_{Cl}, k_{Hp} for the decomposition and dechlorination reaction according to the previous kinetic scheme.
Table 4 reports the activation and the thermodynamic parameters; the error limits are reported in terms of standard deviations.
The partition coefficients, K, at the various temperatures for the OCDF reaction were calculated (Table 5) and their temperature dependency was examined.

5. Discussion and Conclusion

OCDF degradation in a moist nitrogen stream occurs with a complex mechanism involving the combination of various reactions.
The first is a partition of the reactant into two species where one is physically and the other chemically adsorbed on fly ash. The partition is irreversible and temperature-dependent. The isosteric enthalpy of adsorption is about -87 kJ mol^{-1}. The two species react according to two independent reaction pathways.

Table 1 - First-order kinetic constants (min^{-1}) calculated for the disappearance of OCDD and OCDF.

| T (°C) | OCDD | | OCDF | | |
	k ± s.d.	R^2	T (°C)	k ± s.d.	R^2
200 D[a]	$(4.529 \pm 0.850)10^{-3}$	0.651			
200 W[b]	$(2.630 \pm 0.098)10^{-3}$	0.991	200 W[b]	$(1.924 \pm 0.058)10^{-2}$	0.992
300 D[a]	$(1.124 \pm 0.047)10^{-2}$	0.985			
300 W[b]	$(9.820 \pm 0.819)10^{-2}$	0.918			

[a] D = runs with 0 mg H_2O l^{-1}; [b] W = runs with 150 mg H_2O l^{-1}

Table 2 - Formation of the decomposition reaction products

| T (°C) | OCDF | | | OCDD | | |
	C_{Rf}^0/C_R^0	k_D (min^{-1})	R^2	C_{Rf}^0/C_R^0	k_D (min^{-1})	R^2
200	0.5689	$4.706\ 10^{-2}$	1.00			
228	0.9284	$2.059\ 10^{-1}$	1.00			
250	0.9268	$2.377\ 10^{-1}$	1.00			
300	0.9790	$3.162\ 10^{-1}$	1.00	0.7722	$2.103\ 10^{-2}$	0.888

Table 3 - Formation of the dechlorination reaction products.

T (°C)	C_{Ra}^0/C_R^0	k_{Cl} (min^{-1})	k_{Hp} (min^{-1})	R^2
OCDF				
200	0.4311	$9.851\ 10^{-3}$	$3.000\ 10^{-2}$	0.697
228	$7.160\ 10^{-2}$	$6.666\ 10^{-3}$	$3.960\ 10^{-2}$	0.980
250	$7.320\ 10^{-2}$	$4.208\ 10^{-2}$	$1.568\ 10^{-2}$	0.833
300	$2.104\ 10^{-2}$	$7.881\ 10^{-2}$	$2.838\ 10^{-2}$	1.00
OCDD				
300	0.2278	$7.134\ 10^{-3}$	$1.080\ 10^{-2}$	0.506

The OCDF adsorbed physically reacts following a decomposition pathway. The reagent disappearance follows a pseudo first-order kinetics; there is no information about the nature of the hydrodeoxygenation and/or polycondensation reaction products.

The value of $\Delta S^{\ddagger}$ is negative; the absolute value is relatively high. The activation energy (39.5 kJ mol^{-1}) is much lower than the energy required for the thermal dissociation of the C-O bond (at least 430 kJ mol^{-1}) thus indicating that the bond cleavage is assisted by the attack of reactive chemical species.

The chemiadsorbed OCDF reacts following a dechlorination pathway. The reagent disappearance involves first-order series reactions. The data-sets available for product formation make for the reaction scheme integration including only the first two steps: from OCDF to HpCDF

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and the subsequent dechlorination of HpCDF to the lower chlorinated congeners (HxCDF, PeCDF, and TCDF). A good fitting of the experimental data with the curves calculated is obtained. The value of $\Delta S^{\ddagger}$ (Table 4) is negative; the absolute value is relatively high. The activation energy (54.52 kJ mol^{-1}) is much lower than the energy required for the thermal dissociation of the C-Cl bond (at least 400 kJ mol^{-1}) thus indicating that the bond cleavage is assisted by the catalyst and the attack of reactive chemical species.

The values of $\Delta S^{\ddagger}$ calculated for both reactions indicate a "tight" transition state that is more compact and stiffer than the reagent. As a consequence, the reaction products should be adsorbed on the fly ash surface. As for the dechlorination reaction, this is in agreement with the experimental proof that no PCDF/PCDD is detected in the outlet gas of the reactor. The decomposition reaction is still to be tested.

Elaboration similar to that for OCDF regarding OCDD degradation is now not possible for lack of data. However, the treatment of experimental data at 300°C suggests a mechanism similar to that for OCDF. The main difference seems to be in the adsorption of OCDD in fly ash; the partition of the chemiadsorbed OCDD reagent at 300°C is similar to the one calculated for OCDF at 200°C. This may explain why the abrupt variations in PCDD reactivity occur in the temperature range between 300°C and 400°C. Moreover, at 300°C, the influence of water vapor seems to be important as the ratio between the two reaction rates (with and without water vapor) is almost equal to 9.

Finally, according to literature, OCDF in nitrogen is more reactive than OCDD in air.

Table 4 - Activation (from Arrhenius equation) and thermodynamic (from Eyring equation) parameters for the decomposition and the dechlorination reaction of OCDF.

	Decomposition	Dechlorination
ln A ± sd, min^{-1}	7.419 ± 3.796	8.889 ± 5.160
ΔE ± sd, kJ mol^{-1}	39.50 ± 16.23	54.52 ± 22.05
$\Delta S^{\ddagger}$ ± sd, J mol^{-1} K^{-1}	- (230.2 ± 31.74)	- (217.9 ± 42.84)
$\Delta H^{\ddagger}$ ± sd, kJ mol^{-1}	35.17 ± 16.30	50.19 ± 22.01

Table 5 - Partition coefficients at different temperatures

T (°C)	C_R^0 (nmol g^{-1})	C_{Rf}^0/C_R^0	K C_{Rf}^0	C_{Rf}^0 (nmol g^{-1})	K (nmol^{-1} g)
200	24.25	0.5689	0.7578	13.80	5.493 10^{-2}
228	19.38	0.9284	0.0771	17.99	4.286 10^{-3}
250	17.76	0.9268	0.0790	16.46	4.789 10^{-3}
300	26.23	0.9790	0.0214	25.68	8.353 10^{-4}

6. References

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