

KINETIC ASPECTS FROM THE LABORATORY SIMULATION OF THE FORMATION AND DESTRUCTION
OF PCDD/PCDF IN FLY ASH FROM MUNICIPAL WASTE INCINERATORS

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ABSTRACT

Starting from literature data on the laboratory simulation of PCDD and PCDF formation in air and their destruction, under nitrogen atmosphere, in fly ash from MSW incinerators, the formation of PCDD and PCDF congeners was interpreted as independent simultaneous reactions of the pseudo-first order and the kinetic constants were calculated. Furthermore the data of the annealing reaction in nitrogen stream were interpolated using a general kinetic equation.

KEYWORDS

PCDD, PCDF, fly ash catalysis, kinetics, formation, destruction

INTRODUCTION

One of the three general pathways hypothesized to account for the presence of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the gaseous and solid emissions of municipal incinerators is the *de novo* synthesis from organic compounds and sources of chlorine. This pathway was supported by both theoretical (Shaub, 1983) and laboratory (Elceman, 1982; Vogg, 1986, 1987; Stieglitz, 1987; Dickson, 1987; Nestrick, 1987; Hagenmaier, 1987) studies on the catalytic role of fly ash. The mechanism requires the presence of oxygen and metal ions in the reaction system as well as still not clearly identified organic carbon and chlorine sources. Moreover, a decrease of the PCDD and PCDF quantities was observed by thermal treatment in a nitrogen atmosphere (Vogg and Stieglitz, 1987).

The aim of the present work is the formal kinetic interpretation of this phenomenon to try to answer the question: are the kinetic constants of these processes such as to justify the formation of significant amounts of PCDDs and PCDFs in the gaseous and solid effluents of combustion and post combustion within the residence times typical for MSW incinerators?

EXPERIMENTAL

At present our investigation is being carried out only on data concerning laboratory studies conducted at constant temperature, in air or inert gas flow and on untreated fly ash from MSW incinerators. The literature data used to calculate the kinetic parameters for the formation (in air) and destruction (in nitrogen) reactions are reported in Tables 1 and 2.

Table 1 Concentrations ($10^2 \mu\text{mol/kg}$) of PCDD and PCDF congeners for the formation reaction in air at 300°C (Stieglitz, 1987)

t	D4	D5	D6	D7	D8	F4	F5	F6	F7	F8
0	5.59	13.75	14.59	15.76	22.85	39.22	38.19	16.27	10.75	2.93
30	14.29	58.95	104.94	115.25	51.13	104.59	108.69	74.69	63.52	27.04
120	58.42	145.95	263.63	258.73	104.44	451.02	370.13	250.75	171.02	38.31
240	57.49	238.60	422.32	461.01	221.93	382.39	716.76	530.85	381.13	72.11
360	74.58	269.47	473.51	522.17	252.39	509.85	940.02	669.57	459.31	81.12

The hypothesis was made that the process takes place as if the reactions were of the pseudo-first order in homogeneous (solid) phase, i.e., of $R \rightarrow P$ type, at least as far as the rate determining step is concerned. If the PCDD (indicated for simplicity D4 - D8) and

Table 2 Concentrations ($10^2 \mu\text{mol/kg}$) of PCDD and PCDF congeners for the destruction reaction in nitrogen at 300°C (Stieglitz, 1987)

t	D4	D5	D6	D7	D8
60	4.66	3.37	2.56	1.76	1.09
120	1.55	1.40	1.79	0.94	0.87
240	0.62	1.96	1.54	0.71	0.65

PCDF (F4 - F8) congeners were formed from the same reactant R, reactions could be more or less simultaneous but independent. The kinetic equation is Eq. (1)

$$\Delta c = c_P - c_P^0 = c_R^0 - c_R = c_R^0 [1 - \exp(-k t)]$$

Parameters c_R^0 and k_F were determined by a non linear regression.

The data for the destruction reaction were fitted by the general Eq. (2) (Moore, 1981)

$$(c_P/c_P^0)^{1/n} = 1 - (1-n) k_D t$$

The parameters n e k_D were determined using the SIMPLEX method (Seber, 1989). At the moment, Eq. (2) was used only for the fit without any kinetic interpretation.

Table 3 reports the literature data for a run in which a formation reaction, followed by destruction, was observed (Vogg, 1987).

Table 3 Concentrations ($10^2 \mu\text{mol/kg}$) of PCDD and PCDF congeners for the formation and destruction reaction in air at 300°C

t	D4	D5	D6	D7	D8	F4	F5	F6	F7	F8
0	6.22	12.63	21.76	29.46	26.11	36.93	37.89	14.94	11.73	2.7
120	20.20	160.00	419.67	235.21	139.25	165.70	461.49	334.78	251.64	49.13
480	245.49	416.84	899.92	701.15	235.64	1121.4	2040.7	1336.5	888.57	77.97
1320	42.88	60.07	160.74	183.84	110.31	216.36	245.58	244.08	171.02	32.22

RESULTS AND DISCUSSION

The kinetic parameters calculated from Eqs. (1) and (2) are reported in Tables 4 and 5; e.g. some experimental values and calculated curves are shown in Figs. 1 and 2

Table 4. Kinetic parameters from eq.(1)

C_R^0 ($\mu\text{mol}/\text{kg}$)	D4	D5	D6	D7	D8
$10^3 \cdot k$ (min^{-1})	1.21 ± 0.00	3.11 ± 0.14	5.51 ± 0.38	6.45 ± 0.34	4.27 ± 0.10
	F4	F5	F6	F7	F8
C_R^0 ($\mu\text{mol}/\text{kg}$)	8.90 ± 1.01	22.84 ± 0.18	15.06 ± 0.24	8.78 ± 0.35	0.97 ± 0.08
$10^3 \cdot k$ (min^{-1})	1.70 ± 0.00	1.44 ± 0.00	1.65 ± 0.00	1.60 ± 0.00	3.99 ± 0.00

For the reaction of Eq.(1), the available data are the concentrations of the reaction products in the solid homogeneous phase. There are no indications of the nature of the reactants except that a) oxygen and catalytic sites are indispensable to the formation of the products, provided that the reaction time is not too long, b) there are no traces of the reaction products in the gas flow.

Table 5. Kinetic parameters from eq.(2)

n	D4 ^a	D5 ^a	D6	D7	D8
	—	—	3.574	2.324	3.634
k_D	—	—	0.597	0.222	18.49

^a The convergence was not achieved

The results indicate that the formation reactions are not parallel in fact, the concentration proportions of the different congeners are not constant throughout reactions, e.g. $\Delta[D4]/\Delta[D5] = k_4/k_5$. Therefore, the reactant should not be the same in all the reactions which should, consequently, be considered as independent simultaneous reactions.

Fig. 1 Experimental data and calculated curves for the formation reaction of PCDD

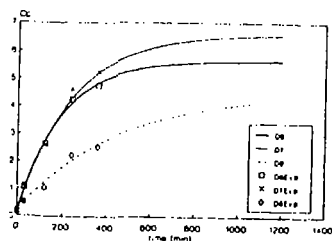
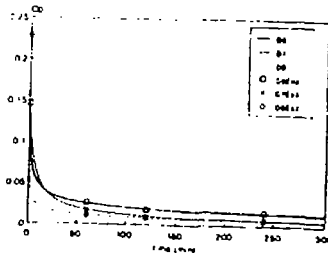


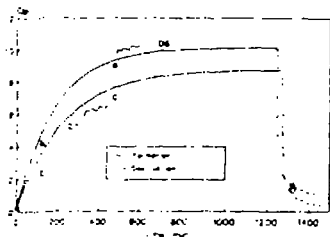
Fig. 2 Experimental data and calculated curves for the destruction reaction of PCDD



In the laboratory studies the concentration c_p of each product starts at "zero time" at some initial value c_p^0 and increases, more and more slowly, to approach a constant value c_p^* asymptotically. This could indicate that at least one of the reactant sources and/or the

processes where both the reactant sources and the catalytic sites, if any, are continuously renewed (Bagnati, 1989). As a consequence, the final fly ash properties should be somewhat different from those resulting from laboratory studies (Pitea, 1989).

Fig. 3 Experimental data and calculated curves for the formation and destruction reactions of PCDD



The calculated k_f and k_d values were used for the interpretation of the data in Table 3. Bearing in mind that the experimental data are very limited, thus giving great uncertainty to the fit (Fig. 3), one can observe that it is not unrealistic to consider that this is a potential model: in spite of the oxygen flow, destruction reactions will start when the reaction sources and/or the catalytic sites are no longer available for the formation. Needless to say, further experimental work is required to confirm this proposal.

Based on the k_f values, it seems realistic that the formation of "significant" amounts of PCDDs and PCDFs in the actual plants can eventually occur only in those points where the contact time between the raw gases and the continuously renewing contact surfaces of the fly ash is of the same order of magnitude as the half-life time which is, in any case, greater than 100 minutes.

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