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KINETICS OF FORMATION OF POLYCHLORINATED DIBENZO-P-DIOXINS/ DIBENZOFURANS FROM CARBON ON FLY ASH

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Key words - Carbon, de novo synthesis, fly ash, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, rate constants.

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Abstract - Experiments were carried out to study the rate of PCDD/F formation from carbon on fly ash. The formation follows first order behaviour during the first part of the experiment. With longer reaction times, degradation reactions become more important. Rate constants found were in between 0.01-0.04 min⁻¹.

1. Introduction

Formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) during the process of waste incineration was discovered in 1977 [1]. Macromolecular carbon has been identified as one of the major sources of the formation of these toxic compounds [2]. This mechanism yielding PCDD/F has been named de novo synthesis. During the formation process the carbon is catalytically oxidized to a number of small organic molecules, a.o. PCDD/F [3]. This reaction takes place on fly ash, small residue particles which are formed in the combustion zone of the incinerator, and brought into the cooling-down zone together with the flue gas [4].

In this article we present data on rate constants of PCDD/F formation during de novo synthesis. With such information available, it will be possible to give a better description of the rate of PCDD/F formation in real incinerators.

2. Experimental

The experimental data used in this article have been described elsewhere [5]. However, this paper contains new interpretations of these data not published before.

Chemicals

The chemicals used in our experiments and in the clean up have been described before [5,6].

Experimental Apparatus

The experimental conditions have been described in ref. [5]. For readers' convenience, we will give a short description of these conditions. Fly ash, from which all organic material had been removed, was mixed with activated carbon. The reaction mixture was heated in a glass tube inside a heating furnace. The fly ash was placed inside the tube as a fixed, packed bed. Experiments lasted for 30-360 min, at a temperature of 300 °C. During the whole experiment, a gas flow composed of air and H₂O was passed through the fly ash bed.

Clean Up and Analysis

These have been described elsewhere [6]. Only the T₄CDD-OCDD and T₄CDF-OCDF were analyzed.

Table I. Amount of PCDD/F homologues formed (in nanomole/g fly ash) as function of the reaction time. (a)

30 min		60 min		120 min		240 min		360 min		
mean	range	mean	range	mean	range	mean	range	mean	range	
0.009	[0.004]	0.013	[0.004]	0.019	[0.009]	0.295	[0.056]	0.326	[0.05]	T ₄ CDD
0.011	[0.004]	0.024	[0.009]	0.031	[0.017]	0.210	[0.036]	0.219	[0.045]	P ₅ CDD
0.009	[0.004]	0.024	[0.012]	0.030	[0.016]	0.141	[0.028]	0.136	[0.041]	H ₆ CDD
0.001	[0]	0.008	[0.004]	0.043	[0.017]	0.022	[0.011]	0.008	[0.004]	H ₇ CDD
0	[0]	0.004	[0.002]	0.011	[0.004]	0.002	[0.001]	0	[0]	OCDD
0.052	[0.023]	0.098	[0.029]	0.127	[0.049]	1.438	[0.317]	1.971	[0.213]	T ₄ CDF
0.027	[0.008]	0.083	[0.03]	0.126	[0.05]	0.988	[0.012]	0.856	[0.124]	P ₅ CDF
0.014	[0.001]	0.061	[0.008]	0.144	[0.059]	0.414	[0.134]	0.210	[0.07]	H ₆ CDF
0.004	[0]	0.015	[0.001]	0.037	[0.012]	0.044	[0.020]	0.017	[0.008]	H ₇ CDF
0.001	[0]	0.004	[0]	0.006	[0.003]	0.006	[0.001]	0.001	[0.001]	OCDF

a: Experimental conditions: 4.0 g fly ash and 0.1 g carbon; 17 ± 0.5 mL/min technical air; T=300 °C; reaction time was varied between 30-360 min; H₂O; all experiments in duplo, mean value ± range is given.

Table II. Rate constants of PCDD and PCDF formation from carbon. (a)

Homologue	Correlation coefficient (r)	rate constants in min ⁻¹
T ₄ CDD	0.93	0.017 ± 0.003
P ₅ CDD	0.91	0.013 ± 0.002
H ₆ CDD	0.89	0.012 ± 0.003
H ₇ CDD	0.94	0.037 ± 0.007
OCDD	0.87	0.030 ± 0.010
T ₄ CDF	0.94	0.016 ± 0.002
P ₅ CDF	0.95	0.016 ± 0.002
H ₆ CDF	0.91	0.014 ± 0.003
H ₇ CDF	0.91	0.024 ± 0.006
OCDF	0.74	0.014 ± 0.007

a: Rate constants were calculated with the data in Table I, using linear regression. The correlation coefficient *r* is shown. For T₄CDD-H₆CDD and T₄CDF-H₆CDF, the concentrations formed between 30-240 min were fitted according to equation (1), for H₇CDD-OCDD and H₇CDF-OCDF, the concentrations between 30-120 min were fitted to equation (1).

3. Results and Discussion

In Table I results are given on the formation of PCDD/F from carbon, taken from ref. [5]. The reaction time was varied between 30-360 min at 300 °C. As PCDD/F are not stable compounds on fly ash, but are subjected to degradation reactions [7], formation and degradation are simultaneous pathways during de novo synthesis. The overall balance will depend on a.o. the availability of carbon and the reaction conditions. As an approximation, we will ignore the degradation reactions and fit the results to a simple first order reaction:

Insight in the mechanism of de novo synthesis is still quite poor and it is not clear what is the character of R. In fact, more than one mechanism could be operative simultaneously, raising some doubt as to the validity of a first order approach. However, the formation of the various PCDD and PCDF homologues can be described with a first order equation quite good. In this equation: R = reactant; R° = concentration

$$\ln R = \ln R^\circ - kt \quad (1)$$

of reactant at *t*=0; *k* = rate constant; *t* = reaction time. A molecule of P (PCDD or PCDF) is formed for every molecule of R that reacts, i.e. we can use the various PCDD/F concentrations to calculate the rate constants. Values of these rate constants and correlation coefficients obtained are presented in Table II. For

the tetra-hexa homologues, rate constants of $0.012\text{--}0.017\text{ min}^{-1}$ are found between 0-240 min. Between 240 and 360 min the concentration of PCDD and PCDF stays more or less the same and the reaction does not follow a single first order equation any longer. After 240 min, the formation reaction levels off and the degradation of PCDD/F formed becomes increasingly important. With the hepta and octa homologues, the degradation reaction sets in earlier and the formation reaction shows first order behaviour between 0-120 min. Our rate constants found ($0.01\text{--}0.04\text{ min}^{-1}$) are higher than those found by Lasagni et al. [8] ($0.0003\text{--}0.007\text{ min}^{-1}$) for de novo synthesis reactions at $300\text{ }^{\circ}\text{C}$.

4. Conclusions

PCDD and PCDF formation from carbon can be described with a simple first order equation during the first part of the experiment. Rate constants of ca. $0.01\text{--}0.04\text{ min}^{-1}$ were found. As the reaction continues, the degradation of the PCDD/F formed becomes important and the overall formation rate now no longer obeys a single first order reaction.

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