

FORMATION OF PCDD/F IN FLY ASH BY ELECTRICAL DISCHARGES.

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are formed during some natural processes and various human activities (1). Considerable efforts have been made to learn more about the formation and destruction of these compounds during combustion (one of the most industrial process leading to PCDD/F formation). Such an information is essential in order to reduce the formation of chlorinated aromatics from combustion processes and, further, to apply appropriate abatement technologies.

The mechanisms of formation of the PCDD/F are not yet well known. About the thermal formation, like in the waste incinerators or others combustion processes, two different pathways are generally accepted (2-9): the 'De Novo' synthesis (from macromolecular carbon present in the fly ash) and the synthesis from precursors (reactions of chemical similar gas-phase compounds, such as chlorophenols).

To avoid the pollution of the air, most of industries, especially iron and steel industries and waste incinerators, use an electrostatic precipitator to eliminate the fly ash present in the gas flow. This system is suspected to be at the origin of the synthesis of PCDD/F but no systematic investigations were performed. In other way, electrical discharges can appear in this kind of apparatus.

The aim of this study was thus to learn the potential formation of PCDD/F in fly ash by electrical discharges. The two different pathways known to date (the 'De Novo' synthesis and synthesis from precursors) were investigated.

Material and Methods

Material :

A high voltage generator, two electrodes and a Faraday cage compose the experimental arc reactor used in the different experiments. The generator gave a variable voltage from 38 to 85 kV (the current is limited to 70 or 150 μ A).

The two electrodes are fixed on plexiglas rings and delimit a little space where it is possible to depose the sample of fly ash to be submitted to the electrical discharges.

Method:

Fly ash samples were submitted to electrical discharges at ambient temperature during 20hrs. After that the PCDD/F were extracted by Soxhlet method with toluene for 24hrs. The extracts were cleaned by acid and basis washes and passed through a chromatographic column of alumina to separate PCDD/F from PCB. The samples were then concentrated in 50 μ l dodecane and analysed by HRGC/HRMS. To quantify the PCDD/F in the different samples, an internal standard consisting of a solution of 13 C-labeled PCDD/F was added to the sample before the Soxhlet extraction. The PCDD/F content of the different samples was expressed in pg/g and was not transformed in pg TEQ/g because many of the PCDD/F congeners were taken in account.

Reagent :

The fly ash samples used were collected in an electrostatic precipitator of a Belgian metal industry. They were used as like as they were received or were previously cleaned by a Soxhlet extraction with toluene (2×24 hrs) to eliminate their important PCDD/F content. 13 C₁₂-labelled PCDD/F (EPA 1613 LCS) were obtained from Campro Scientific (Veenendaal, The Netherlands). All solvents used were p.a grade.

Analysis :

Analysis of PCDD/F were performed by HRGC-HRMS using VG/Fisons-AutoSpec-Q and Hewlett Packard 5890 Series II gas chromatograph (capillary column, 60m, id 0.25mm) with EI at 45 eV and a minimum resolution of 10000 (10% peak valley).

Results and Discussion

1) The De Novo synthesis.

An experiment was carried out in which 13 C enriched carbon was added in the sample before submitted it to the electrical discharges during 20hrs. No standard was added to this sample. PCDD/F with 12 13 C were then researched in the GC/MS analysis. In this study, 10^{20} times more PCDF with 12 13 C than in a natural sample were found. The formation of furans is then obvious.

Considering the expensive cost of isotopic labelled compounds, the comparison of the quantities of PCDD/F in the sample before and after the discharges was investigated to show the De Novo synthesis. The results of the comparative study on cleaned fly ash show that PCDD/F were formed in the electrical discharges.

It is also noticed that the distribution between dioxins and furans is similar to this of the natural sample: the samples content four times more furans than dioxins.

2) The synthesis of PCDD/F from precursors.

Different compounds were tested as precursors of PCDD/F in the electrical discharges: phenol, benzoquinone and four PAH (naphtalene, phenanthrene, pyrene and chrysene).

For phenol as well as benzoquinone, dioxins and furans are formed in the electrical discharges. With phenol, the formation is more important for the PCDD than for the PCDF, contrary to which was found for the 'De Novo' synthesis. The reason of this difference must be found in the mechanism of reaction. Only the mechanism of formation of PCDD from polychlorophenol seems to be obvious. It concerns the condensation of two molecules with elimination of HCl which leads to dioxins and not to furans. For this mechanism, it's necessary to have an orthochlorophenol (with a Cl just next to the OH group). However, authors have shown that isomerisation reactions of chlorophenol(10) can take place in fly ash leading to chlorophenol with a good structure to form PCDD by simple condensation reaction. The presence of a Cl atom at the right place is then not necessary. It's the same for the presence of all the Cl atoms, since authors have shown that chlorination reaction of phenol can take place on fly ash produced in incinerators (11).

About the PAH as precursors, on natural or cleaned fly ash, the formation of PCDD/F can't be made in evidence. The direct synthesis of PCDD/F from these four PAH seems to be not possible under these conditions.

A complementary test was made with phenanthrene to learn if this PAH can undergo modifications in the electrical discharges. Phenanthrene was deposited on silica. NaCl was added to the sample and the mix was submitted to electrical discharges for 20hrs. The purpose of this study was to see if the phenanthrene could be chlorinated in these conditions. The samples were extracted by SFE (CO₂) and the extracts were analysed by GC/MS. The comparison of the spectrum before and after electrical discharges showed that a compound of mass 212 (chlorophenanthrene or benzene 1-chloro 2-phenylethynyl) was appeared due to the electrical treatment. These two compounds could have been formed in the electrical discharges from the phenanthrene.

This complementary test proves that phenanthrene can undergo modifications in the electrical discharges. Chlorination reactions can take place and thus it should not be impossible that toxic compounds such as PCDD/F could be formed. However, PAH should not be direct precursors but the modifications undergone in the electrical

discharges could lead to more efficient precursors. Considering that the phenol is a recognised precursor, these more efficient precursors could be phenolic compounds.

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