

Comparison of Distribution of PCDD/Fs Congeners Generated by PAHs of Different Structures

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Abstract

Study on distributions of 17 noxious congeners generated by PAHs with 6 different structures (300°C, 10% O₂, CuCl₂ as catalyst); the distributions of isomers of PCDD/Fs those are generated by PAHs with different structures in the presence of a catalyst were compared. The comparisons of different structures of PAHs and the distributions of PCDD/Fs isomers generated by these PAHs could provide insights of the mechanism of PCDD/Fs formation by PAHs. It turned out PCDD/Fs generated by these PAHs were dominated by PCDFs (over 80%). PCDD/Fs generated by biphenyl, phenanthrene, pyrene and fluorene with the biphenyl or angularity structure were much higher than those which were generated by naphthalene and anthracene with a linear structure.

Introduction

As products of incomplete combustion, PAHs have been correlated with the formation of PCDD/Fs in previous studies¹⁻³. PAHs could lead to PCDD/F formation under certain conditions; especially they have been shown to have a significant contribution to PCDFs formation⁴⁻⁷. At present, such formation has been suggested mainly through de novo reaction when PAHs are served as the carbon source (PAHs are often perceived as the core of soot)^{6,8}.

The generation of PCDD/Fs from PAHs is greatly influenced by the chemical structures of PAHs; there are great differences in yields of PCDD/Fs and distributions of congeners which are generated by PAHs with different structures. Schoonenboom and Olie⁹ used anthracene in their experiments; a small amount of PCDD/Fs has been measured in the presence of a simulated fly ash as the catalyst. Fullana et al⁵, Wilhelm et al¹⁰, and Stieglitz et al.¹¹ suggested that there is a higher transformation ratio of PCDFs generated from PAHs which have the biphenyl structure and under the condition of a simulated fly ash was used as the catalyst at low temperature. Other PAHs which do not have the biphenyl structure showed relatively low transformation ratios to PCDFs. The experiments were designed to compare the distributions of 17 noxious PCDD/F congeners that are generated by PAHs.

Method

Chemical structures of six PAHs used for the experiments are showed in Fig. 1.

The equipments used in experiments are shown in Fig. 2. A small scale horizontal tube furnace was used as the experimental equipment. Atmosphere is of N₂:O₂=9:1, flow rate at 200 ml/min, and temperature of furnace at 300°C were used in all experiments. The gas existing from the quartz tube was passed through a trap which was filled with XAD-2 SAP. A mixture of CuCl₂·2H₂O (40 mg) and PAHs (20 mg) was weighed and put in a

porcelain boat, which was then covered by quartz sand (2g). The porcelain boat was inserted into the quartz tube after furnace temperature reached 300°C. Each sample operates 30 minutes Extraction and clean-up procedures used the procedures of USA EPA1613. Use HRGC/HRMS to analyze generated PCDD/Fs.

Results and Discussion

1. Yields of 17 noxious PCDD/Fs generated by PAHs with different structures

Congeners of 17 noxious PCDD/Fs which were generated by 6 PAHs are shown in Table 1. The results indicate that PCDFs were the dominating products, which were accounted for 80% of the total PCDD/Fs generated. PCDFs that generated by fluorene, biphenyl and phenanthrene were accounted for 95% of the total PCDD/Fs. PCDFs generated by anthracene and naphthalene were relatively low, but they still reached 81% of the total PCDD/Fs. The observed results suggest that de novo synthesis is the dominating process for generating PCDD/Fs in the presence of a catalyst below 300°C.

As can be observed from Table 1, there are large differences in the amounts of PCDD/Fs generated by different PAHs. Yields of PCDD/Fs generated from biphenyl, fluorene, and phenanthrene were much higher than those generated by naphthalene, anthracene, and pyrene. However, the PCDD/Fs generated from naphthalene, anthracene, and pyrene were of the same order of magnitude. The yields generated from biphenyl were the highest (19, 22, and 38 times to those from naphthalene, anthracene and pyrene, respectively). Yields from fluorene and phenanthrene were higher than those from naphthalene, anthracene and pyrene by one order of magnitude. These observations suggest that the differences in the molecular structures of PAHs have a great influence on their generation of PCDFs.

Comparison of the PCDD/Fs yields produced from six PAHs is shown in Fig 3. There is a biphenyl structure existed in biphenyl, phenanthrene and fluorene; they are easier to generate dibenzofurans in the process of catalytic reaction with biphenyl serves as the building blocks. Biphenyl may take place in the chlorination reaction to generate polychlorobiphenyl, which is then to generate PCDFs. Naphthalene and anthracene don't have such a biphenyl structure, therefore they will generate less PCDFs. Pyrene which has the biphenyl structure, but it generates less PCDFs. There may be a different reaction for those PAHs that have high-number rings such as pyrene. With more oxidation reactions, more bonds between PAH molecule are produced, and finally they are transformed to soot. Soot has high absorbability and low volatility, which is hard to be removed from the surface of catalyst¹². For the porous catalyst, soot blocks the pores which prevent reactants to participate in the catalytic reactions and limit contact of the catalyst with pyrene. Catalytic reaction of pyrene to generate PCDFs is therefore greatly reduced.

2. Comparison of Distribution of PCDD/F Congeners Generated by PAHs with Different Structures

The distributions in International Toxic Equivalence (I-TEQ) of 17 toxic PCDD/Fs generated by six PAHs were different from the distributions of their PCDD/F yields. Fluorene produced PCDD/Fs with the highest toxicity (12,330 ng I-TEQ/g), higher than that produced by biphenyl (Table 1). The distribution of I-TEQ is different from the distribution of total PCDD/Fs, and the main reason is the difference in distribution of PCDD/F congeners. Congeners have different Toxic Equivalence Factors (TEFs), therefore the distribution of I-TEQ is different from the total PCDD/Fs. PCDFs generated by biphenyl are mainly higher-chlorinated furans such as

1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, and OCDF (especially OCDF is the most dominant congener) as shown in Fig. 4, they made up 85.6% of the total PCDFs. These highly chlorinated congeners have low TEFs, the total I-TEQs for PCDD/Fs which are made up mostly by such congeners are therefore also low.

The distributions of toxic PCDD/F congeners shown in Fig. 4 indicate that the structure of PAHs has a significant influence on the distribution of PCDD/F congeners and the fingerprinting of isomers. The distribution of congeners generated by naphthalene is similar to that generated by biphenyl: highly chlorinated congeners such as 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, and OCDF contributed to most of the PCDFs. Fluorene, phenanthrene, and pyrene showed similar distribution patterns, the PCDFs from tetra- to octa-chlorinated congeners were more evenly distributed than those generated from naphthalene and biphenyl. Anthracene generated more highly-chlorinated PCDFs than those generated by fluorene, phenanthrene, and pyrene, which were less than those generated by naphthalene and biphenyl. The differences in distributions of congeners are mainly caused by the differences in reactivity of chemical bond existed in different PAHs structures that lead to changes in degradation, oxidization and chlorination^{6,7} occurring in these structures. The similarity of the distributions of PCDD/Fs generated by fluorene, phenanthrene, and pyrene may be due to the same characteristic of their molecular structures (as biphenyl).

The experiment shows that de novo reaction is the major reaction occurring in the low temperature heating region of a combustion system which leads to PCDD/F formation, and the main formation products are PCDFs. PCDFs generate by fluorene, phenanthrene, and biphenyl accounted for more than 95% of the total PCDD/Fs, they were accounted for 92% in the case of pyrene, and relatively low for anthracene and naphthalene, about 81%.

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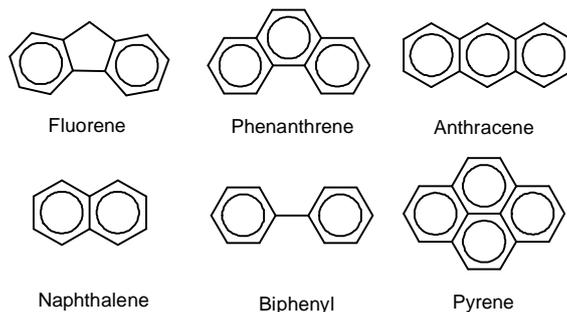


Fig.1 structures of polyaromatic hydrocarbons used in this study

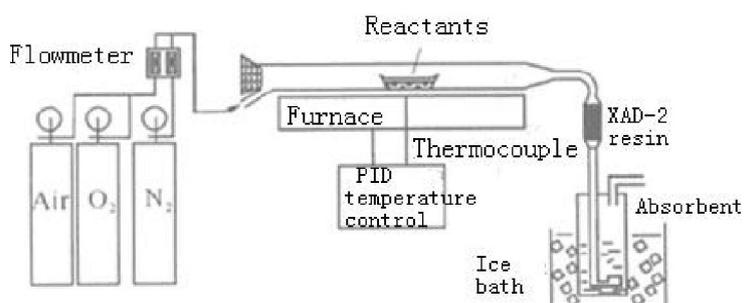


Fig.2 Schematic of experimental system

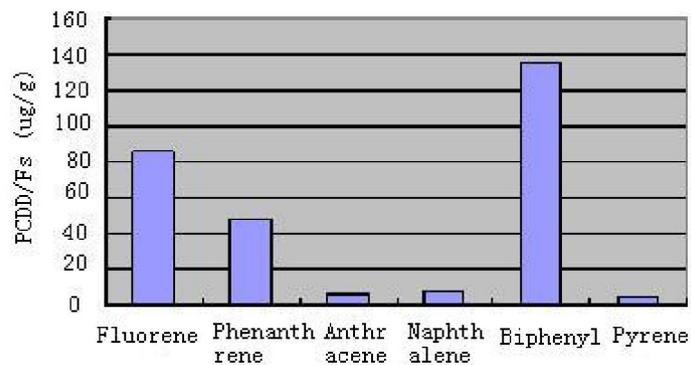


Fig. 3 Total PCDD/Fs yield with different PAH catalysed by CuCl₂

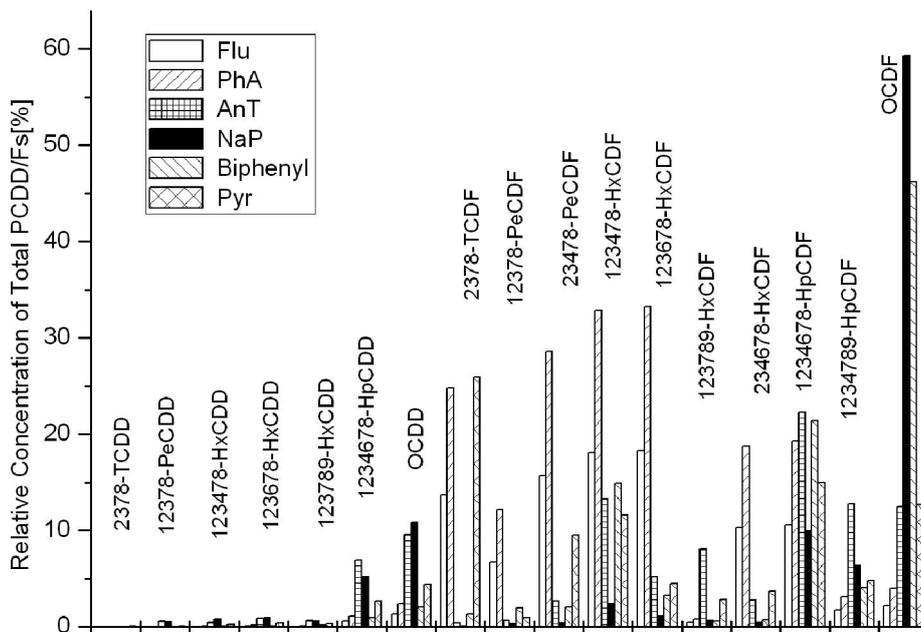


Fig. 4 PCDD/F isomer distribution patterns generated from different PAHs

Table 1

Product yield from catalytic reaction of PAHs(17 most toxic PCDD/F, ng/g)

Reactant	Total PCDD/F	PCDD	PCDF	I-TEQ
Fluorene	85221	1854	83367	12330
Phenanthrene	46977	1564	45413	5201
Anthracene	6289	1206	5083	336
Naphthalene	7312	1382	5930	111
Biphenyl	135489	4790	130699	877
Pyrene	3619	303	3316	369