

FORMATION AND SOURCES - POSTERS

STRUCTURE TYPES OF POLYCYCLIC AROMATIC HYDROCARBONS FROM COMBUSTION PROCESSES

E.S.Brodsky

A.N.Severzov of Institute of Ecology and Evolution RAS, Leninskiy Prospekt 31, 117071 Moscow, Russia

Introduction

Polycyclic aromatic hydrocarbons (PAH) are widespread in the Environment. Benzo(a)pyrene, benzo(a)anthracene, benzofluorantenes and indeno(1,2,3-cd)-pyrene are considered to be most dangerous potential carcinogens.

A typical and very important sources of PAH emission in the Environment is combustion of mineral fuel and organic materials, including industrial and municipal incinerators.

PAH formed due to combustion at high temperature (1700 – 200 K) are mainly unsubstituted compounds of peri-condensed type (pyrenes, benzopyrenes, benzoperilenes, antantrene, coronene etc.). When the combustion temperature decreases the yield of substituted PAH grows. As a rule, it is mainly methyl, polymethyl, ethyl, di- and trialkylsubstituted compounds [1].

PAH distribution adequating to low temperature of the process of their formation, is specified principally by comparatively low molecular PAH with domination of pyrene and phenantrene, concentration of high molecular PAH is rather small. The ratio of phenantrene to anthracene is about 50, and fluorantene/pyrene - about 0,3, as for organic matter in deep sediments during oil formation [1,2]. This picture is also typical for PAH of the oil origin. For high temperature combustion process the ratio Phe/An is less then 10 and the ratio Fluo/Pyr is about 1 [1,2]. Thus, the PAH profile can serve an indicator of their origin.

We have studied the structure types of PAH in gas emissions from industrial incinerator using full scan GC-MS to search some other PAH typical for combustion processes.

Methods and Materials

We studied exausted gases from the furnace LH 750 SC with fuel - natural gas, and the temperature of the second combustion 800[□]. The loading of the furnace was isolated wire, radioplates, radiodetail etc., total mass of the loading was 1 kg, contents of metals 50-70 %, plastics - 50-30 %, size 10 mm. Sampling gas volume was 30-45 m³.

Samples were collected using sampler Staplex TFIA-2 with two filters from a thin silica fibre SKV (diameter about 2 micrometers), first of which served to trap solid particles, and the second filter impregnated by cleaned vaseline served to trap vapours of organics.

The crushed filter placed in the cartridge of the extractor was extracted by 500 mL of hexane-acetone mixture (1:1 v/v). The extract was evaporated for acetone removing and cleaned-up on multilayer column with layers of silica impregnated by acid and alkali. A

FORMATION AND SOURCES - POSTERS

column was eluated with 40 mL hexane-dicloromethane mixture (1:1 v/v), the extract was evaporated up to 30 mL and passed through a microcolumn with charcoal FAS-MD. A column was washed with 20 mL hexane-dicloromethane mixture (1:1), then reversed and eluated with 5 mL toluene at 80°C in opposite direction. Then 45 mL hexane was added to eluate and it was passed through multilayer column with neutral and alkaline silica. A column was eluated with 50 mL hexane, the eluates were combined and cleaned using alumina column, eluted with hexane-dicloromethane mixture (95:5) and (1:1). The last eluate was evaporated to minimal volume and 10 mL n-tridecane was added. The cleaned extract was analyzed using GC-MS instrument MAGNUM (Finnigan MAT). Analysis conditions: a silica capillary column 25 μ m x 0,32 mm with a stationary phase Ultra-2, the temperature was programmed from 100°C (hold 2 min) up to 200°C with the rate 20°C/min, then up to 300°C with rate 5°C/min, injector temperature was 260°C, interface – 220°C, electronic impact ionization at electron energy 70 eV, mass spectra were scanned from 41 up to 500 D (1 spectrum per sec). 2 μ L of the eluate was injected in splitless mode, beginning injector purge through 0,5 min.

Identification of aromatic compounds was performed using chromatographic retention times and mass spectra (molecular ions, isotope cluster and fragmentation routs. Naturally the identification should be considered as proposal.

Component concentrations were evaluated using internal standard. In Tab.1-2 the identified PAH and estimated concentration are given.

Results and discussion

There was found out a number of various aromatic compounds. The results have shown, that aromatic hydrocarbons is possible to systematize on their structure as follows:

- Kata-condensed PAH: anthracene (178), tetracene (228), etc.
- Peri-condensed PAH: fluorantene (202), pyrene (202), benzofluorantene (252), benzopyrenes (252), etc.
- Linear PAH: biphenyl (230), quaterphenyl (306), diphenylmethane (168), dinaphtylphenylmethane (218), dinaphtylmethane (268) etc., The main structural PAHs found are shown in Scheme 1.

Fragmentation of the compounds of binuclear type (biphenyl, binaphtyl, phenylnaphtyl etc.) is characterise by elimination H or 3H with following cyclisation. As for the compounds with methylene bridge they eliminate CH_2+2H with cyclisation of the resulting ion.

Apparently, under certain conditions linear PAH are the basic compounds of this class in combustion products (Table). This supervision is obviously important to view that they can be intermediate products for formation of condensed PAH. Yield of pericondensed PAH is much less than kata-condensed that points to comparatively mild combustion conditions.

It is interesting that chlorinated pyrenes were not found in these samples while they are the main type of chlorinated PAH in the products of high temperature combustion.

In one of the samples chlorinated PAH practically were not found out (though PCDDs and PCDFs are available). In another sample a number of chlorinated PAH was found

FORMATION AND SOURCES - POSTERS

(mainly, monochlorinated), including chlorinated linear PAH. Previously chlorinated linear PAH were found in breast milk from Bashkiria [3].

It points that processes of catalytic chlorination of PAH are occur. In this sample some brominated and chloro- bromo substituted PAH were found - chlorinated and brominated dibenzodioxin and dibenzofurans, and also bromophenanthrene.

There is not direct relation between linear aromatics (including chlorinated) and PCDD/PCDF formation, but they can be transformed to polychlorinated PAH condensed type like chlorinated diphenyl ethers are considered as precursors of chlorinated dibenzofurans.

It should be noticed that chlorinated linear PAH were found in breast milk from Bashkiria [3]. Linear PAH such as biphenyls and terphenyls were found in incinerator combustion products [4], polychlorinated diphenyl ethers – in ashes [5].

Therefore linear PAH are very representative compounds for mild combustion processes and can be used for differentiation of the sources of PAH in the Environment.

Acknowledgments

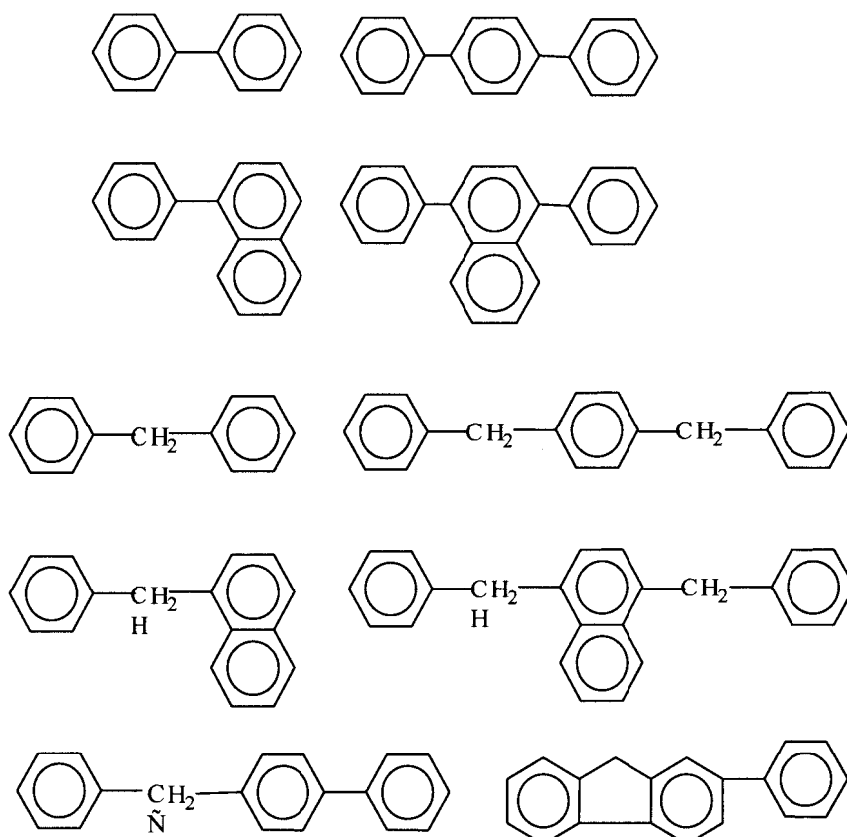
This work was supported by INTAS Association Project 96-1990.

References

1. P.Garrigues, H.Budzinski, X.Michel, J.F.Narbonne,. Abstracts of the third international symposium TOCOEN'96, Lunacoviche, Czech Republic, 1996, pp.89-98.
2. Catallo W.J., Chemosphere, 1998, v. 37, No. 1, pp. 143-157.
3. Brodsky E.S., N.A.Klyuev, V.S.Soyfer, L.K.Karimova and G.G.Maximov. 1995. Chlorinated aromatic compounds in breast milk and foodstuffs from Bashkiria. Proceedings of the Conference "Dioxins: ecological problems and analytical procedures", Ufa, 1995, pp.63-67.
4. Bumb R.R., Crummett W.B., Cutie S.S., Gredhill J.R., Hummel R.H., et al., Science, 1980, v.210, N.4468, pp.385-389.
5. Paasivirta J., Tarhanen J., Soikkeli J., Chemosphere, 1986, v.15, pp.1429-1433.

FORMATION AND SOURCES - POSTERS

Scheme 1. Structure types of linear PAHs.



Table

Types of PAH in the industrial incinerator gas emissions (ng/m^3)

PAH types	Sample 1	Sample 2
Kata-condensed PAH	327	65
Peri-condensed PAH	19	<1
Linear PAH	537	497
Chlorinated kata-condensed PAH	<1	67
Chlorinated peri-condensed PAH	<1	<1
Chlorinated linear PAH	<1	8+126(PCBs)
PCDD/PCDFs ($\text{Cl}_2 - \text{Cl}_8$)	19	300