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Formation of Polychlorinated Naphthalenes on Fly Ash

M. Schneider, L. Stieglitz, R. Will, G. Zwick

Institut für Technische Chemie, Bereich Chemisch-Physikalische Verfahren

Forschungszentrum für Technik und Umwelt Karlsruhe GmbH

Postfach 3640, D-76021 Karlsruhe, Germany

1. Introduction

Polychlorinated Naphthalenes, PCN ($C_{10}H_{8-x}Cl_x$ or Cl_xN , $x = 1-8$) are a class of 75 congeners. PCN have been used mainly as dielectric fluids, insulation materials, flame retardants, fungicides and pesticides, as addition in oils and plasticizers.¹⁾

PCN exhibit similar chemical and physical properties like polychlorinated biphenyls (PCB).

Therefore PCN are widespread and persistent industrial pollutants in the environment. Furthermore they resist chemical and biological degradation and accumulate in our environment. Some of the isomers of PCN are known to be strongly bioaccumulating and showing dioxinlike toxic properties such as chloracne and liver damages.¹⁻⁶⁾

There are three main sources of PCN: Technical mixtures of Cl_xN , this is the main input in the global environment. PCN are also found in trace amounts as by-products in technical PCB-mixtures. Another important source is the formation of PCN during incineration processes like waste incineration (MWI) or incineration of coal in power plants.^{1,3,5)}

The aim of this study was to develop an isomerspecific analysis of PCN in technical mixtures (Halowax[®]) on fly ash and to investigate their formation on fly ash.

2. Experimental

Halowax[®] (1000, 1001, 1099, 1014), different Cl_xN - and ¹³C-PCB-standards were purchased from Promochem (Wesel, Germany). Standardsolutions were prepared in toluene.

In our study we used fly ash collected from an electrostatic precipitator from a municipal waste incinerator (MWI) with a content of 4.2% carbon.

5 g of this fly ash were soxhlet extracted with toluene for 20 h after addition of ¹³C-PCB as internal standards to quantify the PCN originally present on the fly ash.

To investigate the formation and degradation of Cl_xN on fly ash by thermal treatment the fly ash was used without former cleaning, e.g. extraction with organic solvents to avoid formation of artefacts.⁷⁾ 5 g of fly ash were heated at 300° C for 0.5, 1, 2, 4 h in a vertical tube of borosilicate glass, with the fly ash on a porous glass frit. During the annealing a stream of synthetic air (50 ml/min, containing 150 mg water vapour / l air) was passed through the apparatus and afterwards through XAD-tubes in series, containing 200 mg XAD-16 each to trap volatile Cl_xN .

After the thermal treatment the fly ash was brought into a soxhlet, and after addition of ^{13}C -labelled PCB-standards extracted with toluene for 20 h. The XAD was eluted with toluene and dichloromethane.

Finally extract and eluate were cleaned up and separated by liquid chromatography on superactive basic alumina oxide with hexane : dichloromethane (9 : 1) as fraction 1, hexane : dichloromethane (1 : 1) as fraction 2. Most of the PCN and PCB were eluted in fraction 1, only trace amounts could be detected in fraction 2. Remarkable was the detection of 1,6,7- and 2,3,6- Cl_3N (only in fly ash to be found in greater amounts) in fraction 1 and 2 in nearly the same amounts. Therefore fraction 1 and 2 were united in one fraction for the quantification of PCN because no interferences were to be expected with other organic chlorine compounds found on fly ash such as PCDD/F, PCBz, PCPh.

Identification and quantification was achieved by a combination of GC-MSD (HP 5890) using a DB5 (length 30 m, i.d. 0.25 mm, phase 0.25 μm) coupled by a MSD (HP 5970).

In the multi-ion detection mode (MID) using the both most intensive and characteristic ion masses from the molecular ion region for each level of chlorination Cl_xN and $^{13}\text{C}\text{-Cl}_x\text{B}$ were measured.

3. Results and Discussion

Technical PCN-mixtures are produced by chlorination of molten naphthalene with chlorine gas in the presence of FeCl_3 and / or SbCl_5 as catalysts till a desired chlorine content is reached. Depending on the Cl-content different Cl_xN dominate in the technical PCN-mixtures like Halowax[®].¹⁾

Table 1: Cl-content of different Halowaxes and dominant grade of chlorination in Cl_xN

Halowax:	Cl-content	chlorination degree Cl_xN
1000	26 %	x = 1,2
1001	50 %	x = (1,2) 3,4 (5)
1099	52 %	x = (1,2) 3,4 (5)
1014	62 %	x = (3) 4,5,6 (7)

According to the mechanism of an electrophilic substitution, all Halowaxes show a specific pattern of Cl_xN -isomeres.

On fly ash there are mainly Cl_2N , Cl_3N , Cl_4N , Cl_5N and Cl_6N to be found, because Cl_1N evaporates easily and Cl_7N , Cl_8N degradates under thermal conditions found in incineration processes. The specific pattern of Cl_xN formed by incineration in a de-novo-synthesis is totally different from that found in Halowaxes.

Table 2: Blank value of Cl_xN on fly ash

Cl_xN	Cl_xN [ng/g]	Cl_xN	Cl_xN [ng/g]
Cl_1N	19	Cl_3N	87
Cl_2N	36	Cl_6N	32
Cl_3N	60	Cl_7N	5
Cl_4N	84	Cl_8N	0,4

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During the thermal treatment at 300° C Cl₁N - Cl₆N were formed on fly ash in higher amounts. The data are given as net concentration (total-blank) in table 3. Cl₁N - Cl₃N were also found in the gasphase trapped by XAD, because of their volatility at 300° C, Cl₄N - Cl₆N could be found in the gasphase only in little amounts. After 2 h annealing time most of the Cl_xN reached their maximum of formation. Cl₄N (1603 ng/g) and Cl₅N (1355 ng/g) followed by Cl₃N (1074 ng/g) and Cl₂N (818 ng/g) were formed most. Cl₆N (287 ng/g) were formed less, but noteworthy is the high formation of 1,2,3,4,6,7-/1,2,3,5,6,7-Cl₆N (251 ng/g), because 1,2,3,5,6,7-Cl₆N is known as a strongly bioaccumulating PCN and shows dioxinlike toxic properties.^{4,6)}

Table 3: Formation of Cl_xN by annealing fly ash at 300° C
(sum of compounds on fly ash and XAD trap)

React. time [h]	Cl ₁ N [ng/g]	Cl ₂ N [ng/g]	Cl ₃ N [ng/g]	Cl ₄ N [ng/g]	Cl ₅ N [ng/g]	Cl ₆ N [ng/g]	Cl ₇ N [ng/g]	Cl ₈ N [ng/g]
0,5	102	294	292	386	352	98	0,4	< 0,1
1,0	93	393	572	878	750	190	2	< 0,1
2,0	170	622	967	1604	1355	287	< 0,1	< 0,1
4,0	131	818	1074	1570	1252	240	< 0,1	< 0,1

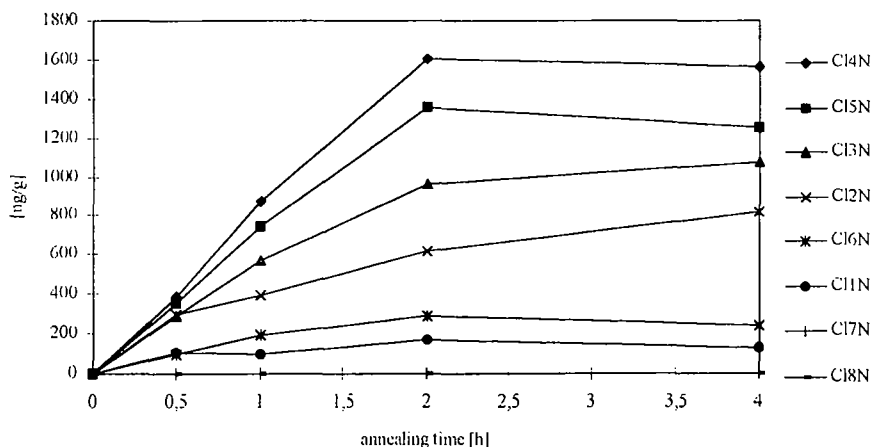


Figure 1: Formation of Cl_xN by annealing fly ash at 300° C

A comparison of the isomers of the congener groups in Halowax mixtures and in the thermally treated fly ash shows a distinct difference. The most prominent isomers formed in the two matrices are shown in table 4.⁸⁾ The data indicate different formation mechanisms between the electrophilic substitution with chlorine in presence of FeCl₃ and the de-novo-synthesis in fly ash.^{9,10)}

Table 4: Dominant Cl_xN in Halowax and fly ash (most dominant **isomers** are in bold letters, less dominant (isomers) are in brackets, most toxic isomers are underlined)

Cl _x N	Halowax	flyash
Cl ₁ N	1	2
Cl ₂ N	14/16	(13), 12, 23, (18)
Cl ₃ N	(136), 146 , 145	135, 137, 125, 126, 127, 167/236 , (138)
Cl ₄ N	1257/1246/1247 , 1467, 1235/1358, 1248, 1268 , 1458	1367, 1368/1256 , 1237, 1234, 1267 , 1258/2367, (1238)
Cl ₅ N	12468 , 12456, 12478, 12358, 12458	12356, 12367 , (12368)
Cl ₆ N	123578/(123568), 124568/124578 , 123458	123467/123567 , (123678)
Cl ₇ N	1234568	1234567

4. References

- 1) Brinkman U.A.T., H.G.M. Reymer (1976): Polychlorinated Naphthalenes
J.Chromatgr. 127, 203-243.
- 2) Rathen H. (1975): Chlorkohlenwasserstoffe, aromatische, kernchlorierte
Ullmanns Enzyklopädie der technischen Chemie, H. Ullmann 9, 499-524.
- 3) Pearson C.R. :Halogenated aromatics, Environmental chemistry, Vol. 3, Part B, Anthropogenic
compounds, O. Hutzinger.
- 4) Williams D.T., B. Kennedy. G.L. LeBel (1993): Chlorinated naphthalenes in human adipose tissue
from Ontario municipalities. Chemosphere 27, 795-806.
- 5) Sanderman W. (1974): Polychlorierte aromatische Verbindungen als Umweltgifte.
Naturwissenschaften 61, 207-213.
- 6) Asplund L., B. Jansson, G. Sundström, I.Brandt, U. Brinkmann (1986): Characterisation of a strongly
bioaccumulating hexachloronaphtalene. Chemosphere 15, 619-628.
- 7) Mandl B., L. Stieglitz (1993): Formation of organic compounds from toluene with fly ash as catalyst.
Chemosphere 27, 179-186.
- 8) Takasuga T., T. Inoue, E. Ohi, P. Ireland (1994): Development of an all congenere specific,
HRGC/HRMS analytical method for polychlorinated naphthalenes in environmental samples.
Organohalogen compounds 19, 177- 182.
- 9) Schwarz G., L. Stieglitz (1992): Formation of organohalogen compounds in fly ash by metal-
catalyzed oxidation of residual carbon. Chemosphere 25, 277-282.
- 10) Stieglitz L., G. Zwick, J. Beck, W. Roth, H. Vogg (1989): On the de-novo-synthesis of
PCDD/PCDF on fly ash of municipal waste incinerators. Chemosphere 18, 1219-1226.