

Formation of Brominated Compounds on Fly Ash

D.Heinbuch, L. Stieglitz
Institut für Heiße Chemie
Kernforschungszentrum Karlsruhe mbH
Postfach 3640
7500 Karlsruhe / FRG

Abstract

In fly ash from a municipal waste incinerator the inorganic chloride was substituted by bromide to contain 10-30 wt% bromide. By a thermal treatment of the fly ash in air at 300°C (1 hr.) a variety of aromatic bromocompounds is formed, e.g. bromobenzenes, -benzonitriles, -thiophenes, -naphthalenes, -dibenzofurans. The yield depends on the content of the added bromide.

Introduction

By the metal-ion-catalyzed reaction of residual carbon with inorganic chloride on fly ash not only PCDD/PCDF are formed in a de-novo-synthesis but also other classes of organochlorine compounds, e.g. chlorbenzenes, -thiophenes, -benzonitriles, -biphenyls, -naphthalenes, -benzofurans and -benzothiophenes.

Additionally in bromide-chloride containing systems mixed chloro-bromocompounds were identified [1,2]. In order to study the role of bromide in this reaction we substituted in a specific preparation step chloride by bromide without changing the residual composition of the fly ash. The influence of the bromide concentration on the yield of different compound classes was studied under standard annealing conditions (300°C, 1 hr., air).

Material

The fly ash was taken from the elektrofilter system of a MWI. It was homogenized and refluxed twice for 12 hours with toluene. After filtering the residue was dried 3 hours at 70°C under reduced pressure (30 mbar).

Fly ash preparation

The fly ash was treated with water (bidest) until chloride (proved as AgCl) could not be detected anymore. To make sure that other ions (metal salts, especially copper) essential for the de-novo-synthesis are not removed a sample of treated fly ash was refluxed 12 hours with

water and the filtered water was analyzed for heavy metals by AAS (Perkin Elmer 2380/2100). As Tab. 1 shows no evidence was found for a leaching of heavy metals into the water.

Tab. 1 : Concentrations of Heavy Metals in Untreated Fly Ash and in Wash Water in ppm

Conc. (ppm)	Cu	Fe	Ni	Zn	Pb	Cd	Sn	Ca	Mg	Na	K
Wash water	<0.01	6.8	<0.01	<0.01	0.08	<0.01	23	522	1.7	2040	3750
Fly ash	1000	22000	21	14000	12000	26	2000	28000	11000	25000	41000

Bromide (10/20/30 wt%, as KBr) was added to portions of 20 g of the treated fly ash mixed in a rotation evaporator for 3 hours at 50°C and dried at 80°C under reduced pressure (15 mbar).

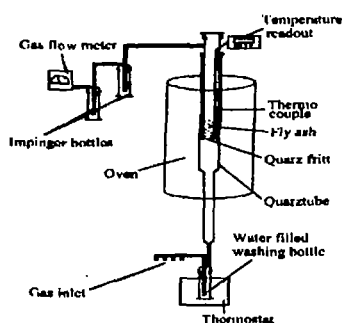


Fig. 1 : Experimental setup for thermal treatment

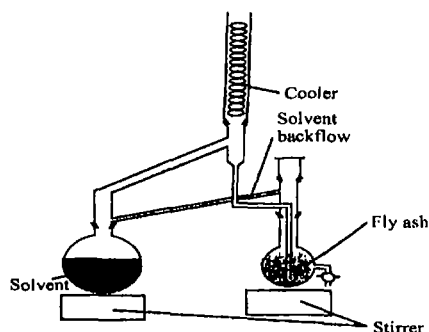


Fig. 2: Extraction method

Thermal treatment

Fly ash samples of 10 g each were heated in a furnace (Fig. 1) for one hour at 300°C. The temperature of the fly ash sample was measured by a thermocouple to $\pm 5^\circ\text{C}$. During thermal treatment a stream of synthetic air (50 ml/min) containing 120 mg of water vapor per liter was passed through the samples. To ensure close contact between the gas phase and the fly ash the sample was placed in a quartz tube with a frit at the bottom using an ascending gas flow. At the gas outlet of the arrangement two impinger bottles were installed to trap volatile compounds, the first containing 100 ml benzene and the second the same amount of cyclohexane.

Sample preparation

The treated fly ash was digested with 60 ml of 1N HCl, the residue centrifugated, washed two times with water and freeze dried. The weight loss of the fly ash by this procedure was determined by weighing to be about 60%. The residue was extracted 24 hours with 250 ml of benzene and 24 hours with 250 ml of cyclohexane. To avoid chemical reactions on the surface of the fly ash, we used a setup (Fig. 2) described in [2]. By this method the solvent temperature in the extraction flask was adjusted to 40°C.

Clean up

For quantitation the solutions were concentrated to about 500 µl. Fractionation into two parts was carried out by semipreparative high performance liquid chromatography using a RP18 column (250 mm length, 10 mm i.d.) and methanol as mobil phase. Fractionation was time-controlled, because brominated compounds are UV-sensitive and UV-detection cannot be used.

Analysis

GC-MS was performed on a Carlo Erba gaschromatograph with splitless on column injection on an uncoated precolumn (5m) connected to a DB5 column (30m length, 0.25 mm i.d., 0.2 mm filmthickness) using helium as carrier gas. The temperature programm was : 3 minutes isothermal at 80°C, 5°/min to 220°C, 10°/min to 300°C, 30 minutes isothermal. A Finnigan Mat mass spectrometer with an Incos data system operated in EI-Mode was used at 1s/cycle.

Identification of the compounds was carried out by retention time, isotope ratio of the parent masses and by the mass spectra. Tetrafluorodibromobenzene was used as internal standard.

Results

Bromide (wt%)	10	20	30
Benzenes	22451	34050	54440
monobromo-	2319	6099	9752
dibromo-	11351	11010	15577
m-dibromo-	881	909	1179
p-dibromo-	365	602	258
o-dibromo-	10105	9499	14140
tribromo-	5190	7741	12067
tetrabromo-	2773	6917	12308
pentabromo-	818	1999	4671
hexabromo-	n.d.	284	65
Thiophenes	53	1657	1449
monobromo-	6	69	408
dibromo-	47	369	242
tribromo-	n.d.	637	388
tetrabromo-	n.d.	582	411
Naphthalenes	204	779	223
monobromo-	111	140	87
dibromo-	93	327	131
tribromo-	n.d.	190	5
tetrabromo-	n.d.	122	n.d.

Bromide (wt%)	10	20	30
Benzonitriles	1377	2876	1745
monobromo-	757	477	546
3-monobromo-	114	136	21
4-monobromo-	51	39	11
2-monobromo-	592	302	514
dibromo-	83	708	414
tribromo-	33	982	544
tetrabromo-	504	701	241
pentabromo-	n.d.	8	n.d.
PBrDF	794	1547	239
monobromo-	320	202	99
dibromo-	308	392	74
tribromo-	166	561	66
tetrabromo-	n.d.	327	n.d.
pentabromo-	n.d.	65	n.d.
Σ Sum	24879	40909	58087

Tab. 2 : Concentrations (ng/g) of Brominated Compounds Formed on Fly Ash in Dependence of Bromide Concentration

Tab. 2 shows the concentrations of different brominated compounds as the sum of all degrees of bromination depending on the concentration of bromide.

Because bromide was not present in the modified fly ash the formation of brominated compounds can be explained by de-novo-synthesis from residual carbon and the added bromide. This is supported by the increase of TOX (Total organic halogen) during thermal treatment ($\Delta\text{TOX} = 150 \mu\text{g/g}$).

The formation of brominated compounds increases with the concentration of bromide, bromobenzenes being the most favoured and determining substance class. The quantitative ratio between the different classes of substances is comparable to the results obtained on untreated fly ash (containing 5% chloride) [2]. The highest concentrations are found for the di- and trisubstituted species. A closer look at the pattern of the three dibromobenzenes shows a preference of the ortho-position (o/m+p - 10/1). This is a hint for a two-stage mechanism of bromination of the residual carbon on the fly ash surface. The first step is a bromination of the carbon surface yielding side by side orientation. The second step is the oxidative decomposition of the carbon particle separating side by side substituted species, see [3]. The pattern of the monobromobenzonitriles shows a similar behaviour as the dibromobenzenes. The preference of 2-bromobenzonitrile (bromide in ortho-position to cyanide) indicates that cyanide (as a pseudohalogenide) reacts in the same manner like halogenides in the de-novo-synthesis.

In summary the formation of halogenated organic compounds on fly ash by de-novo-synthesis is not restricted to chloride. Other halogenides (bromide) or pseudohalogenides (cyanide) reacts in the same manner by a two-stage mechanism.

Literature

- [1] L. Stieglitz, G. Zwick, J. Beck, H. Bautz, W. Roth, Chemosphere 19, 283-290, (1989)
- [2] G. Schwarz, L. Stieglitz, W. Roth, Dioxin 90, Bayreuth, FRG 1990
- [3] G. Schwarz, Dissertation 1991