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Effects of oxygen on formation of PCB and PCDD/F on extracted fly ash in the presence of carbon and cupric salt

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Abstract

The effect of oxygen–nitrogen atmosphere ($N_2 + 10\%O_2, N_2 + 1\%O_2$ and 99.999% N_2) on the formation of PCB, PCDD and PCDF by the de novo synthetic reactions in the system consisting of extracted fly ash (from municipal waste incinerators – MWI), activated carbon, $CuCl_2 \cdot 2H_2O$ and NaCl at 340°C was studied. The content of PCDD/F for systems with 10% O_2, 1%O_2 and 99.999% N_2 was decreasing and corresponded to 17304, 5544, and 1437 ng/sample. In all studied systems the isomer OCDD/F was prevailing. The content of PCBs in the same system was also decreasing from 1214 to 166 ng/g. Formation of nonortho PCB was relatively high compared to the system where only nitrogen was present. The possible mechanism of formation is outlined. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fly ash; de novo synthesis; PCB; PCDD; PCDF; Activated carbon; Cu(II)Cl_2; NaCl

1. Introduction

There exists evidence that catalytic reactions (the so-called de novo synthesis, de novo synthetic reactions) within the range of 200–350°C on the surface of fly ash particles in the postcombustion zone of a municipal waste incinerator (MWI) play an important role in the formation of highly noxious halogen-containing persistent organic pollutants (POPs) such as PCB, PCDD and PCDF.

Radical, gas–solid phase reactions taking place in the vicinity of the combustion chamber are not kinetically favored as compared to fly ash-mediated heterogeneous reactions proceeding at relatively low temperatures. However, these reactions strongly depend not only on operational conditions but also on the presence of compounds, which could function as potential precursors for these synthetic reactions. These facts present important reason on why the results of different authors are sometimes contradictory. An essential prerequisite condition for the de novo synthetic as well as for dechlorination reactions is the presence of transition or heavy metal cations, reactive carbon and source of chlorine and also the presence of oxygen in the reaction atmosphere.

The de novo synthetic reactions were studied at laboratory conditions on the basis of the knowledge of PCB and PCDD/F formation on fly ash in incinerators in the presence of carbon (Addink et al., 1991; Stieglitz et al., 1997), carbon and inorganic chlorine (Addink and Olie, 1993) and with the added copper(II) chloride (Stieglitz et al., 1989; Weber et al., 1999). Similar studies were also executed on model fly ash with matrix component of Mg–Al-silicate (Sakai et al., 1996; Hell et al., 1997; Stieglitz et al., 1994).

With regard to the fact that the presence of oxygen is a significant factor for execution of the de novo synthetic reactions, formation of PCB and PCDD/F was studied

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at different oxygen concentrations and in the nitrogen atmosphere in the system fly ash-activated carbon–NaCl– $CuCl_2 \cdot 2H_2O$ at 340°C.

2. Experimental

Fly ash from fabric filter of MWI CKD-Purotherm (type PL8/100) was used. The main chemical components of the fly ash were Al 5.96, C 8.24, Ca 4.4, Fe 9.8, Mg 0.38, Si 33.96, Zn 0.2 and water 2.41 all in wt%. Cr 0.21, Ni 0.36, Cu 0.15 and Pb 0.45 all in mg/g. Mercury density was made 1.03 g/m^3 and the calculated porosity was equal to 0.57. Fly ash was soxhlet-extracted with toluene for 24 h, then air dried and sieved to 0.25 mm particle size.

Chemicals. Mixtures of $N_2 + 10\%\ O_2, N_2 + 1\%\ O_2$ and N_2 of 99.999 purity were supplied by Linde. Certified NaCl and $CuCl_2 \cdot 2H_2O$ were of Lachema p.a. purity. Activated carbon for chromatography (Merck, 35–50 mesh ASTM), toluene 99.5%, A.C.S. spectrophotometric grade (Aldrich) and 2-ethoxyethanol p.a. (Fluka) were used.

Experimental arrangement. The well-homogenized mixture of fly ash (0.44 g), NaCl (0.428 mmol), $CuCl_2 \cdot 2H_2O$ (0.064 mmol) and carbon (1.998 mmol) was prepared. Flow rate of gases through this system was made 10 ml/min. The experimental unit is illustrated on Fig. 1. The gases were bubbled through the impinger with water at laboratory temperature (for the system with N_2-99.999 only this step was eliminated), were mixed in the mixing box, preheated to about 300°C and introduced to the U-shaped reaction tube fixed in an oven, which was heated to 340°C. The inner diameter of the inlet part was made 5 mm and of the outlet part 10 mm. The bottom of U-shaped tube was filled with glass gravel on which in the outlet part was the layer of the reaction mixture. The gas pipes were thermally insulated up to the inlet to two ice-cooled liquid absorbers filled with 2-ethoxyethanol. Before the start of the experiment the system was thoroughly washed with gases for 30 min, then it was heated to 340°C (30 min) and kept at this temperature for another 60 min.

3. Analytical methods

The isotope dilution method was used for determination of PCDD/F. Internal standard method was applied for PCB determination. The samples of fly ash were soxhlet-extracted with toluene after HCl pretreatment. Then the solvent was changed to hexane. The 10% aliquot was analyzed. The sequence of clean-up steps was used for removal of co-extracts (US EPA, 1990). $GCQ^{(TM)}$ (Finnigan MAT, San Jose, CA, USA) gas chromatograph coupled with ion trap with external ionization was used with $GCQ^{(TM)}$ 2.2 software version. MS/MS methods of detection were used to achieve corresponding selectivity and sensitivity. Full-scan method of detection was used for quality analyses of precursors. DB-5 ms fused silica column (60 m (length) × 0.25 mm ID × 0.25 μm film) was applied. The DB-17 column (30 m (length) × 0.25 mm *ID* × 0.25 μm film) was used for confirmation of concentrations of some toxic congeners of PCDD/F.

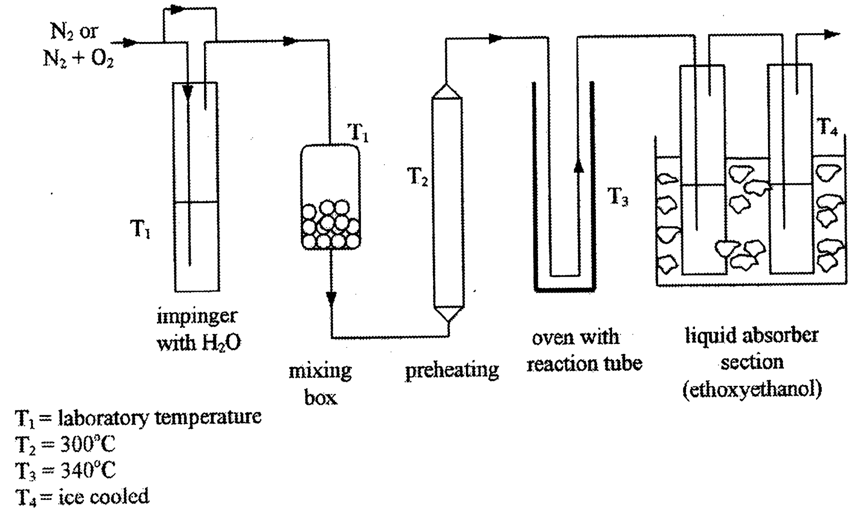

Fig. 1. Experimental unit.

4. Results and discussion

4.1. The reaction system

The system with the effect of oxygen and nitrogen atmosphere on de novo synthetic reactions was chosen so as to enable to study most thoroughly not only synthetic but also dehalogenation reactions that might have taken place. These conditions are best satisfied by systems where predominantly highly chlorinated compounds would be formed. This is the reason why higher concentrations of $CuCl_2$ were used which favor formation of octa- and hepta-chlorinated isomers. The NaCl present acts probably only as a chlorinating agent when no other chlorine sources are available (Addink et al., 1998a; Lenoir et al., 1998). The disordered carbon structure in the fly ash plays an important role for the de novo synthetic reactions (Stieglitz, 1998). For these reasons activated carbon was added into the system as many authors do in studies of de novo synthetic reactions on model fly ash.

The selected reaction components also limit the formation of phenol precursors. At the given composition of the reaction mixture and at the temperature of 340°C formation of chlorinated benzenes exceeds 30 times the rate of formation of chlorinated phenols, while higher concentrations of $CuCl_2$ might destroy the chlorophenols as well (Hell et al., 1997; Addink and Altwicker, 1998b). The temperature of 300–340°C seems to be optimal, as according to literature data, no Deacon reactions can occur and no elemental chlorine is taking part in the chlorination process (Addink et al., 1991; Stieglitz, 1998).

4.2. Polychlorinated dibenzo-p-dioxins and dibenzofurans

The results of formation of PCDD and PCDF at 340°C in the atmosphere of $N_2 + 10\%\ O_2$, $N_2 + 1\%\ O_2$ and 99.999% N_2 are presented in Table 1.

The results prove that reduction of oxygen content up to pure nitrogen atmosphere causes tremendous

Table 1
Formation of PCDD and PCDF by de novo synthetic reaction in different oxygen and nitrogen atmospheres (concentrations in ng/sample)

Isomer	$N_2 + 10\%\ O_2$	$N_2 + 1\%\ O_2$	N_2
2378TCDD	1.51	2.93	0.381
12378PeCDD	29.7	12.1	2.28
123478HxCDD	34.4	12.7	2.61
123678HxCDD	38.5	13.6	2.13
123789HxCDD	41.7	19.6	3.35
1234678HpCDD	341	109	22.3
TCDD	50.3	50	14.6
PeCDD	193	123	30.2
HxCDD	543	234	48.9
HpCDD	728	256	58.8
OCDD	3140	443	76.9
$\sum$ PCDD	4654	1106	229
2378TCDF	18.4	10.5	2.99
12378PeCDF	51.7	38.1	6.98
23478PeCDF	124	40.3	10.4
123478HxCDF	253	98.9	31.1
123678HxCDF	231	111	26.9
234678HxCDF	394	101	27.3
123789HxCDF	6.13	2.96	0.756
1234678HpCDF	3440	1010	233
1234789HpCDF	117	33.0	7.33
TCDF	1130	672	216
PeCDF	1730	1030	317
HxCDF	3110	1210	345
HpCDF	4110	1200	279
OCDF	2570	326	50.7
$\sum$ PCDF	12650	4438	1208
$\sum$ PCDD/F	17304	5544	1437
Ratio PCDD/PCDF	0.37	0.25	0.19

decrease in PCDD/F formation. In all cases PCDF are dominant reaction components. The PCDD/PCDF ratio, which is considered to be a highly sensitive indicator of reaction conditions, decreases from 0.37 to 0.19 when going from the oxygen rich to nitrogen atmosphere. Stieglitz (1998) found the ratios of 0.75 and 0.25 for the Mg–silicate matrix and the same system excluding fly ash at comparable conditions. On the other hand, in systems where no Cu(II) compound was present the PCDD/PCDF ratios are very low (0.1–0.3) and are decreasing even to <0.03 at oxygen deficient conditions (Addink et al., 1991; Addink and Olie, 1993; Stieglitz et al., 1997). The PCDD/PCDF ratio of 0.43 for oxygen rich atmosphere and for the system containing only activated carbon, $CuCl_2$ and KCl were calculated from Weber et al. (1999) data. This ratio and the fact that no fly ash was present in the studied system clearly shows how important the presence of carbon is in the system for de novo synthetic reactions.

With dioxins the concentration of PCDD is decreasing step by step in all systems from octa- to tetra-chlorinated dioxins. In the case of dibenzofurans in the system $N_2 + 10\%\ O_2$ HpCDF, in the system $N_2 + 1\%\ O_2$ HxCDF and HpCDF are prevailing which is probably due to significant dechloration of OCDF and HpCDF taking place. In the nitrogen rich atmosphere obviously further dehalogenation of OCDF and HpCDF take place with prevailing HxCDF isomers. These facts have proven that the de novo synthetic and dehalogenation reactions are of competitive character, without regard if dechloration of primary formed highly chlorinated compounds has taken place or if these compounds were formed by coupling of chlorinated precursors especially of chlorinated benzenes and phenols.

Addink and Olie (1993) studied also the de novo synthetic reactions in dependence on concentration of oxygen; however, no Cu(II) salt was added into the reaction system. In pure nitrogen atmosphere almost no PCDD/F formation was observed, while in the presence of 1% O_2 a drastic increase of PCDD/F was found as compared with the data for the system where 10% of O_2 were present. These results are not in agreement with our findings for similar systems, however, taking into account the fact that in our experiments $CuCl_2 \cdot 2H_2O$ was added. The results of Weber et al. (1999) in air atmosphere where only $C + CuCl_2$ was present in the reaction system have demonstrated that under these conditions practically only OCDD/F and HpCDD/F were formed. Their results prove the fact that one of the very efficient agents for transporting inorganic chlorine into carbon structure seems to be Cu(II)-salts. Still it is not clear if $CuCl_2$ functions more as a chlorine source rather than as a catalyst (Addink and Altwicker, 1998b).

4.3. Polychlorinated biphenyls

The results of formation of PCB at 340°C in the atmosphere of $N_2 + 10\%\ O_2$, $N_2 + 1\%\ O_2$, and 99.999 N_2 are presented in Table 2. For the oxygen rich conditions the HxCB are mostly formed where coplanar PCB (nonortho PCB169 and monoortho PCB 156) are in highest concentrations. Under conditions of reduced oxygen concentration the tetra-CB and PeCB are the predominant isomers with higher content of nonortho PCB 81 and 77 with a very high content of the most toxic nonortho PCB 126. Our findings are in a fairly good agreement with the data of Ling and Hon (1998) where their data for nonortho PCB on fly ash (MWI) are decreasing in the series $\text{PCB126} < \text{PCB169} \ll \text{PCB 77}$. However, in our experiments the concentration of PCB 169 is equal to the concentration of PCB 77. The results of Sakai et al. (1996) for municipal solid waste combustion, where the concentrations of coplanar PCB are at reduced oxygen concentrations (3% O_2) much higher than at higher O_2 concentration (9.6%) differ from our findings. The formation of decachlorobiphenyl in 99.999% nitrogen decreased 54-times and of octa- and nonachlorobiphenyls 42-times as compared with results for the system of $N_2 + 10\%\ O_2$. In the oxygen rich atmosphere the prevailing formed isomers are hexachlorobiphenyls, however, in the nitrogen atmosphere the prevailing component are tetra- and pentachlorobiphenyls. Dechlorination reactions are probably the main reasons for these results, as has been already stated before.

In pure nitrogen, the concentrations of PCB 77 and 126 have considerably increased from 4.3% to 11.5% and from 8.3% to 12.2%, in comparison with experiments under the oxygen rich atmosphere. This fact is in agreement with the general knowledge that small combustors with incomplete combustion generate coplanar PCB at much higher concentrations as in modern incineration plants with strictly controlled combustion regime.

4.4. General comments

On the basis of the results obtained in the studied system which we might understand as a system where dehalogenation and de novo synthetic reactions are competing, we can schematically outline the following model for the main steps of chlorine transfer from its inorganic form to the organic one and vice versa.

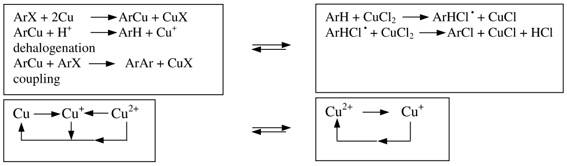

Table 2
Formation of PCB by de novo synthetic reaction in different oxygen and nitrogen atmospheres (concentrations in ng/sample)

Isomer	I-TEF	$N_2 + 10\% \ O_2$		$N_2 + 1\% \ O_2$		N_2	
		ng/sample	TEQ	ng/sample	TEQ	ng/sample	TEQ
TrCB		12.1		205		15	
PCB81	0.0001	12.5	0.0013	9.7	0.0010	6.5	0.0007
PCB77	0.0001	52.3	0.0052	35.5	0.0036	19.1	0.0019
$\sum$ tox. TeCB		64.8	0.0065	45.2	0.0046	25.6	0.0026
$\sum$ TeCB		102.7	0.0065	232.2	0.0046	47.6	0.0026
PCB123	0.0001	12.4	0.0012	6.3	0.0006	2.7	0.0003
PCB118	0.0001	20.3	0.0020	11.9	0.0012	3.8	0.0004
PCB114	0.0005	13.5	0.0068	5	0.0025	0	0
PCB105	0.0001	28.5	0.0029	14.5	0.0015	3.4	0.0003
PCB126	0.1	101	10.1	44	4.4	20.2	2.020
$\sum$ tox. PeCB		175.7	10.1	81.7	4.4	30.1	2.0
$\sum$ PeCB		194.22	10.1	126.5	4.4	46.1	2.0
PCB167	0.00001	17.9	0.0002	5.3	0.0001	1.8	0
PCB156	0.0005	68.9	0.034	22	0.011	6	0.0030
PCB157	0.0005	33	0.016	7.9	0.004	2.3	0.0012
PCB169	0.01	56.9	0.57	19.5	0.195	8.05	0.0805
$\sum$ tox. HxCB		176.7	0.62	54.7	0.21	18.2	0.0850
$\sum$ HxCB		265.9	0.62	179.4	0.21	32.4	0.085
PCB189	0.0001	68.9	0.007	11.3	0.0011	3.6	0.0004
$\sum$ HpCB		174.4	0.007	44.2	0.0011	14.5	0.0004
OctaCB		151		24.6		3.6	
NonaCB		161		23.4		3.8	
DCB		153		19.5		2.8	
Total PCB		1214	10.7	855	4.6	166	2.1
Nonortho PCB		223	10.7	109	4.6	54	2.1
Monoortho PCB		263	0.071	84	0.022	24	0.006

In the oxygen rich atmosphere the direct transfer of halogen is suggested, which is schematically demonstrated by radical aromatic substitution forming radical intermediate. However, according to Stieglitz (1998), the second stage of electron transfer oxidation and loss of proton yields the product ArCl which points to an electrophylic aromatic substitution reaction. Such type of reaction has been described for phenol chlorination in the presence of $CuCl_2$. If no oxygen is present the chlorination stops because Cu(I) chloride is highly retarding the chlorination process. Thus only the Cu(II) → Cu(I) cycling must be anticipated (Crocker and Walser, 1970). The decrease of products formed by the de novo synthetic reactions found in our experiments in the oxygen deficient systems as the consequence of insufficient quantity of Cu(I) compounds which are repeatedly oxidized might be the explanation of this phenomenon. This fact can be supported by Stieglitz et al. (1996) experiments. However, such types of reactions have been experimentally proven also on silico–alumina, silicagel, and Tenax GC polymer supports impregnated by copper chloride in the presence of carbon (Olie et al., 1998). The PCDD/PCDF ratios and these facts prove the idea that the matrix seems to be of negligible importance for the de novo synthetic reactions.

In the nitrogen atmosphere the dehalogenation or coupling reactions can occur, however, the Ullmann reactions should be of crucial importance. Chlorinated biphenyls are formed according to the Ullmann reaction I and can be converted to dibenzofurans in the presence of oxygen. The Ullmann reaction II yields halogenated diphenylethers, where their oxidation produces hydroxylated diphenylethers leading to the ring closure and PCDD formation (Tuppurainen et al., 1998; Stach et al., 1999).

According to Stieglitz (1998) transfer of chlorine into the carboneous structure and the following oxidative degradation of this structure are efficiently catalyzed by Cu(II). Here the decisive role is played by carbon with a polymeric disordered structure called particulate carbon, where from the NMR measurements (Huang et al., 1999) aromatic carbon, and oxidized functional groups are present (carbonyl, ketones, esters, oxygen and sulfur linkages between graphitic carbon layers, oxygen heteroatoms within the graphitic carbon sheet). These findings could explain why PCB, PCDD/F were formed in our experiments even under conditions where only 99.999% N_2 was used. Thus, the synthetized compounds correspond probably only to oxygen which was present in fly ash and activated carbon before experiment and which could have been utilized for oxidation of Cu(I) to Cu(II) and thus for formation of experimentally detected amounts of PCB and PCDD/F formed.

5. Conclusions

- In all studied systems concentrations of PCDD/F were distinctly decreasing going from oxygen rich atmosphere to pure nitrogen.
- In all systems concentrations of PCDF were higher as compared with PCDD.
- In the atmosphere with reduced oxygen concentration the tetrachloro and pentachloro-biphenyls are the predominant isomers with high content of PCB 77, PCB 81 and PCB 126.
- The isomer composition seems to be the product of competition of the de novo synthetic and dechlorination reactions.

Acknowledgements

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