CHLORINATION OF DIBENZOFURAN, DIBENZO-P-DIOXIN AND ACTIVATED CARBON DURING DIGESTION OF SAMPLES IN BOILING 10 % HCL

Alfons Buekens[1], Peter Brown[2], Klaus Jay[3]

[1] Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium, E-mail: abuekens@vub.ac.be
[2] Tasmanian Electro Metallurgical Co., PO Box 164, George Town Tasmania 7253, Australia
[3] Forschungszentrum Karlsruhe (FZK), ITC-CPV, Postfach 3640, D - 76021 Karlsruhe, Germany

Introduction

Six samples, collected during dioxin reduction trials at the TEMCO manganese ore fines sintering plant in Bell Bay, Tasmania, were analysed for PCDD/F and other compounds. During analysis only 40% of PCDD/F was recovered after two consecutive toluene and xylene Soxhlet extractions. The added standards of chlorophenol and pyrenes were strongly adsorbed and those of penta- and hexachlorobenzene and perylene disappeared even entirely. To improve their recovery the mineral matrix was dissolved by boiling the sample in a solution of 10% HCl. Results are surprising, since sample digestion in HCl in particular for PCPh, but also for PCDF, PCBz, PCB (not for PCDD!) gives rise to much higher values (up to 800x; Table 1, Table 2). Digestion in other boiling acids (10% H_2SO_4 or 10% HNO_3) fails to produce similar effects (Table 3).

Thus a new formation route of chlorinated aromatics is observed. Digestion in HCl generates PCDD/F with pronounced non-thermal fingerprint: a high ratio of 2,3,7,8-substituted congeners, relative to their corresponding isomer group. Two hypotheses are: a mix of boiling HCl + MnO_2 either chlorinates aromatic structures pre-adsorbed on coke, or cyclic structures in coke are subject to destructive chlorination. Dedicated experiments show that both formation routes are possible: activated carbon and a mixture of dibenzofuran (DF) and of dibenzo-p-dioxin (DD) were treated under the same conditions as used during digestion of dust samples, and the resulting PCDD/F were analysed. The PCDD/F capacity of MnO_2, Fe_2O_3 and PbO_2 is experimentally compared.

Methods and Materials

The original six samples are: (1) Metallurgical Ore Fines, mainly consisting of pyrolusite (MnO_2), hausmannite (Mn_3O_4), hematite (Fe_2O_3), α-quartz, and other minerals, (2) three coarse fractions from the ElectroStatic Precipitator (ESP) discharge, (3) two samples of fine filter dust, taken from the hoppers under Field 1 and 2, and representative for ESP fines under good sampling conditions. The dust samples typically contain 10 % coke, ore, and volatile elements (S, Cl, Pb, P, K, Mo, Fe).

Test Procedures: 1) mixture of 1g Merck Activated Carbon (AC) + 10g MnO_2 is boiled for 3h under complete reflux in 150ml of a 10% HCl solution. Afterwards AC is extracted, and PCDD/F, PCB, PCPh, PCBz, are determined; 2) mix of 100µg DD + 100µg DF + 5g MnO_2 is treated as above with boiling HCl. Only PCDD/F is expected, possibly with products of oxidative or chlorinating breakdown. Other oxidants have been tested: 5g Fe_2O_3 and 5g PbO_2 replacing 5g MnO_2.

Results and Discussion

Samples analysed after Soxhlet extraction only (Old values)

The *old values* from the original Soxhlet extraction-based analysis are given in Table 1. Depending

on the trial, coarse dust has low values and fine dust is higher in load. The PCDD/PCDF-ratio is low (0.2 – 0.35) and the molar level of chlorination comparable to MSW-incinerator fly ash. Manganese Ore fines have an atmospheric fingerprint (OCDD and HpCDD, no PCDF detected).

Samples analysed after digestion in HCl (new values), H_2SO_4 and HNO_3

Samples after digestion in HCl (new values) markedly increase in I-TEQ: the already high field 1 and 2 values rising by 3 to 5.6, but lower values multiplied by 16 to 475. Also PCB, PCBz, and especially PCPh become much higher in the new analyses. Table 2 shows the ratio of new to old values. PCDD-values, however, rise only marginally, on average by 1.32 (range 0.82 – 1.96). Logically, the test was then repeated with other boiling solutions of mineral acids, namely 10% H2SO4 or 10% HNO3. The results are slightly higher than those after extraction only (Table 3).

Results of Digestion in Boiling HCl on Activated Carbon, DD and DF (Table 4)

To check the mechanism of formation the same treatment is now applied to Activated Carbon, and also to a mix of 100 µg DD + 100 µg DF. Moreover, MnO_2 is compared as an oxidant to Fe_2O_3 and to PbO_2. Treating 1g AC yields almost negligible (wt./wt. PCDF: 10^{-7}; PCDD: 10^{-9}) amounts of PCDD/F (P = 4 to 8), but yields of treating DD + DF are low to fairly high (0.089 to 30.3%, Table 3). PCDF and I-TEQ yields rise in a sequence of oxidising power: AC << Fe_2O_3 < MnO_2 < PbO_2, whereas the proportion of PCDD in PCDD/F varies from 0.3 to 5.0 % in the series: PbO_2 < AC < MnO_2 < Fe_2O_3. Apparently the strongest oxidant deeper destroys PCDD. For the level of chlorination of PCDD there is a sequence: Fe_2O_3 << MnO_2 < AC = PbO_2. Unfortunately, there is no MCDD to TrCDD Data! For PCDF it is: AC < Fe_2O_3 < PbO_2 < MnO_2

The fingerprint of Soxhlet-extracted and samples digested in boiling H_2SO_4 or HNO_3 conforms to the thermal fingerprints from MSW-incineration and metallurgical processes. Those from HCl digestion show much more 2,3,7,8-substituted congeners, and more low chlorinated PCDF and high chlorinated PCDD, indicating that the mechanism of formation is distinct from thermal. Average chlorination level decreases substantially for PCDF, yet increases for PCDD. The data are also compared to those from synthetic samples tested. The result is disappointing, for each of the synthetic systems yields a distinct fingerprint, which is also different from that in HCl digestion.

Formation of PCBz, PCPh, PCB from AC. Testing the AC-route yields: 20 – 60 µg PCBz (P = 2 – 6), 16.0 µg PCPh (P = 2 – 5) and 1.4 – 3.2 µg PCB (P = 2 – 10) per g Activated Carbon. Average weight chlorination levels are very low for PCBz, medium for PCB, and very high for PCPh.

Discrimination between mechanisms: Carbon Chlorination vs. Aromatics Chlorination

Applying the yields from activated carbon (Table 4) to the coke in TEMCO dust allows predicting product generation during HCl treatment. The result fits quite well (Table 7). Only PCBz is too low, by a factor 10 - 200. Ore is the other outlier, producing e.g. 30 times too much PCPh. This is readily explained, however, by its much higher oxidation potential! Coarse dust is often lower.

In the second hypothesis DD/DF chlorination is responsible for PCDD/F formation. Required DD/DF amount is easily estimated as 31 ng DD and 368 ng DF per g dust. These amounts are about two orders of magnitude lower, than independent VUB estimates based on desorption tests.

Hence, both pathways seem possible. Fingerprints from AC fit better, but still imperfectly, with the fingerprint found, digesting dust samples in boiling HCl. The fit from direct DD/F chlorination with MnO_2 is much worse, but it can be argued that the presence of coke and dust again may have influenced upon this fingerprint. However, although both AC and DD/F reacted under the same experimental conditions, there are some deep differences to be pointed at: (1) assimilating AC to coke, oxidised in the sintering bed and activated by the presence of KCl, $PbCl_2$... is a hazardous extrapolation and (2) it is unproven and even unlikely that DD/F react similarly in boiling HCl as the same compounds occluded and adsorbed in the pores of coke and dust!

Conclusions

During digestion of dust samples in boiling 10% HCl an unusual formation route of chlorinated aromatics was observed, dramatically increasing the original dust load: PCPh is multiplied by 35 – 800, PCDF by 2 – 100, PCBz by 1.8 – 36, PCB by 3 – 18, but PCDD only by 0.8 – 2. Digestion in boiling 10% H_2SO_4 or HNO_3 fails to produce comparable results. HCl-digested samples get markedly enriched in lower chlorinated 2,3,7,8-substituted PCDF and higher chlorinated PCDD. Two hypotheses are tested: either the mix of boiling HCl + MnO_2 chlorinates aromatics adsorbed on coke, or destructive chlorination of coke takes place.

When AC is treated in HCl 20 – 60 µg PCBz, 16 µg PCPh, and 1.4 – 3.2 µg PCB is formed, together with 227 ng PCDF and 4.5 ng PCDD. Assimilating 1 g Carbon in TEMCO dust to 1 g AC, the additional amount of these compounds potentially formed from 1g of Carbon is readily computed and the resulting amounts agree well with experimental ones, except the PCBz.

However, direct chlorination of pre-existing DF/DD is also plausible, since the required amounts of DD/DF are probably far exceeded in the dust, following estimates from other work on thermal desorption of organics from dust. Unfortunately, it is unclear in how far AC is similar to coke-in-dust, or boiling DD and DF in HCl can mimic their treatment, while adsorbed in dust pores!

PCDF and I-TEQ yields and chlorination levels of DF rise in a sequence of oxidising power: $Fe_2O_3 < MnO_2 < PbO_2$. However, the strongest oxidant also deeper destroys PCDD.

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Table 1. I-TEQ load of Ore Fines and TEMCO ESP Dust, March 2002 dust data

	Ore Fines	ESP Dust* High Inhibitor	ESP Dust* High inhibitor/No recycle	ESP Dust* Low inhibitor	ESP Dust Field 2	ESP Dust Field 1
PCDF Old, pg/g	0	461	455	3600	73900	114900
PCDF New, pg/g	2050	23900	41200	32700	304800	252000
Old pg I-TEQ/g (Nato)	0.32	14.4	14.9	96.4	2310	3070
New pg I-TEQ/g (Nato)	152	1260	3630	1550	12900	9380
Ratio New/Old TEQ	**475**	**87.6**	**244**	**16.1**	**5.57**	**3.1**

Table 2. Multiplier (Ratio New/Old, no units), after digestion in a boiling 10% HCl solution

	Average Value	Ore Fines	High inhibitor	High inhibitor No recycle	Low inhibitor	Field 2	Field 1
PCDD	1.32	1.22	1.96	1.40	0.82	1.09	1.42
PCDF	31.6	Very high	51.9	90.6	9.08	4.12	2.19
PCBz	14.4	2.48	35.6	35.2	6.86	1.80	4.56
PCPh	293	Very high	337	803	240	50	34.5
PCB	6.95	3.07	4.93	18.4	5.31	4.88	5.13

Table 3. Average Results from the 4 Preparation Methods, Basis 100 = 10 % H_2SO_4

Parameter	PCDD	PCDF	of the 7 TEQ PCDD	of the 10 TEQ PCDF	I-TEQ	Molar Average Chlorination Level	
						PCDD	PCDF
Extraction	77	77	80	71	84	6.57	5.87
Boiling in 10% HCl	112	4040	144	1615	11215	7.07	4.60

Boiling in 10% H_2SO_4	100	100	100	100	100	6.57	5.97
Boiling in 10% HNO_3	86	137	87	88	106	6.57	6.03

Table 4. Yields obtained in various Tests

Test System	10g MnO_2+1g AC	5g MnO_2+100µg DD/F	5g Fe_2O_3+100µg DD/F	5gPbO_2+100µg DD/F
PCDD, wt./wt.	4.52 x 10^{-9}	5.28 %	1.28 %	0.089 %
PCDF, wt./wt.	226.8 x 10^{-9}	20.0 %	2.44 %	30.3 %

Table 5. The (molar) level of chlorination of PCDD and of PCDF

Test System	10g MnO_2+1g AC	5g MnO_2+100µg DD/F	5g Fe_2O_3+100µg DD/F	5gPbO_2+100µg DD/F
Chlor. PCDD	5.7	5.4	4.1	5.8
Chlor. PCDF	4.2	5.3	4.7	4.9

Table 6. Products formed from AC: yield and molar average chlorination level

Compound	PCDD	PCDF	PCBz (P > 1)	PCPh (P > 1)	PCB (P > 1)
Amount, ng/g Activated Carbon	4.52	227	20000 / 60000	16000	1400 / 3200
Molar Level of Chlorination	5.7	5.4	2.2 /2.3	4	3.5 / 4.3

Table 7. Comparison of Predicted Values and Experimental Values, %, AC Hypothesis

	Min., %	Max., %	Average, %	Legend
PCDD	(11)	1400	390	PCDD, PCDF, PCBz, PCPh and PCB formation estimated assuming 1 g of Carbon in the Coke = 1 g Activated Carbon. The computed result is compared to the actual analytical value. One outlier is discarded: PCPh in the ore. This value is a factor 300 too high, possibly due to strongly oxidising conditions in ore without coke. ( ) = computed value is negative
PCDF	58	950	350	
PCBz	0,55	9,5	3,2	
PCPh	60	275	173	
PCB	8,8	250	64	

Table 8. Original Concentration Values Required, Chlorination of Aromatics Hypothesis

TEMCO Dust	Min.., ng/g	Max., ng/g	Average, ng/g	Legend: the amount of DD and DF, required to form the experimental PCDD/F values during digestion, are computed for each sample
DD, ng/g	(2)	165	32	
DF	10	1150	386	

Table 9. Hagenmaier Fingerprint for PCDF

	No HCl, Range[*], %	HCl Digested, SD %	Mindip Fingerprint[2], %
2.3.7.8-TCDF/sum TCDF	7.1 - 8.2	38.3 +/- 1.6	2 - 7
1.2.3.7.8-PeCDF/sum PeCDF	9.2 -11.6	17.9 +/- 6.2	2 - 20
2.3.4.7.8-PeCDF/sum PeCDF	10.5 - 12.2	23.7 +/- 9.2	5 - 14
1.2.3.4.7.8-HxCDF/sum HxCDF	26.6 -27.6	37.8 +/- 9.7	6 - 24
1.2.3.6.7.8-HxCDF/sum HxCDF	13.4 - 15.12	15.6 +/- 2.1	8 - 13
1.2.3.7.8.9-HxCDF/sum HxCDF	4.0 - 5.1	3.3 +/- 1.6	5 - 15
2.3.4.6.7.8-HxCDF/sum HxCDF	1.7 - 3.0	3.2 +/- 0.6	0,1 – 1.2
1.2.3.4.6.7.8-HpCDF/sum HpCDF	40.4 - 58.2	47.0 +/- 3.5	63 - 90
1.2.3.4.7.8.9-HpCDF/sum HpCDF	12.0 - 18.9	27.7 +/- 5.8	1.5 -10
OCDF/sum PCDF	15.7 - 23.3	3.7 +/- 3.1	n.d.

[*] No digestion, or with 10% H_2SO_4 and 10% HNO_3; average of 3 samples

[2] Data from industrial Dust Samples + de novo tests on them. There is no statistical difference between both groups. The range given is Average +/- Standard Deviation.