PCDF FORMATION FROM DIBENZOFURAN IN ARTIFICIAL BRINE

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Introduction

The electrolysis of alkali salt solutions is believed to be a potential formation source for polychlorinated Dibenzodioxins (PCDD) and Dibenzofurans (PCDF). Few analytical data are available in the literature [1-4] mostly for residues of this process indicating that nearly exclusively PCDF are formed in this process with a dominance of the 2378-substituted congeners creating a unique "chloroalkali-electrolysis" pattern. It is assumed that the source is non-chlorinated Dibenzofuran (DBF) which undergoes a subsequent chlorination forming the PCDF during the electrolysis and that the tar used as binder in graphite electrodes is the origin of the DBF. No data are available to our knowledge proving this mechanism. The investigation of the electrolysis process by adding DBF under controlled conditions and study the formation mechanism of PCDF can help to clarify this assumption.

Materials and Methods

Reagent grade sodium chloride was dissolved (25% by wt.) in de-ionized and carbon treated water. This solution is referred to as "ultra-pure" brine. The ultra-pure brine was spiked with Dibenzofuran (DBF) and treated in laboratory electrolysis cells under different conditions:

treatment at 20ºC for 0.1 h
treatment at 20ºC for 1 h
treatment at 50ºC for 1 h

The targeted DBF starting concentration was 1 ppb.

The anolyte of the laboratory cells was sampled and analyzed for all polychlorinated Dibenzodioxins (PCDD) and polychlorinated Dibenzofurans (PCDF) from Mono – through OctaCDF. The DBF content was measured in the samples of the treated brine as well as DBF in the untreated ultra-pure brine.
All samples were analyzed with HRGC/HRMS in Dow's Trace Laboratory following a modified EPA 1613b procedure. In addition to extraction standards listed in the EPA method all samples were spiked with ^{13}C-labelled DBF and one ^{13}C-PCDF- and ^{13}C-PCDD-standard for each chlorination degree from Mono- through TriCDF.
A DB5-MS column (30m x 0.25mm i.d. x 0.25µm) was used for the determination of the PCDD and PCDF. The congeners were identified either with available labeled or unlabeled standards or with the relative retention times derived from Fishman et al.[5]. Some congeners are not separated on the DB5-MS column and are reported as sum of the co-eluting components.

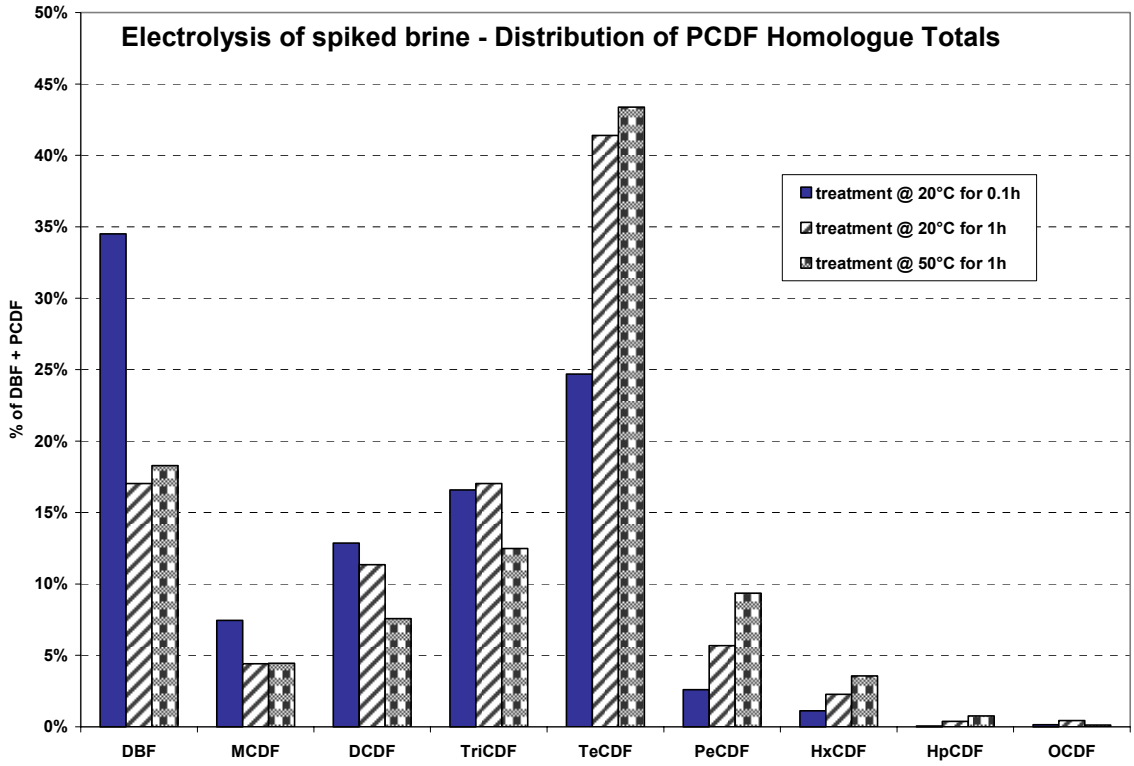
Initial method blank analysis showed substantial background levels of DBF in some of the laboratory solvents used for analysis as received from suppliers. This required specialized cleaning of glassware and freshly distilling solvents used for this investigation.
For a better comparison of the data all experimental results are normalized to the total amount of DBF+PCDF in each experiment.

Results and Discussion

None of the analyses showed detectable amounts of PCDD therefore the evaluation of the data will be limited to the PCDF.
DBF and PCDD/F were not detected in the untreated ultra-pure brine.

The homologue totals profiles for all experiments are shown in Figure 1.
PCDF could be detected in all experiments. Depending on the experimental treatment conditions of the ultra-pure brine the spiked DBF was converted to PCDF at a reaction yield between 65 and 80 %. Total TCDFs were determined to be the major homologue totals in all experiments. Higher chlorinated PCDF are also detectable but at significantly lower concentrations.

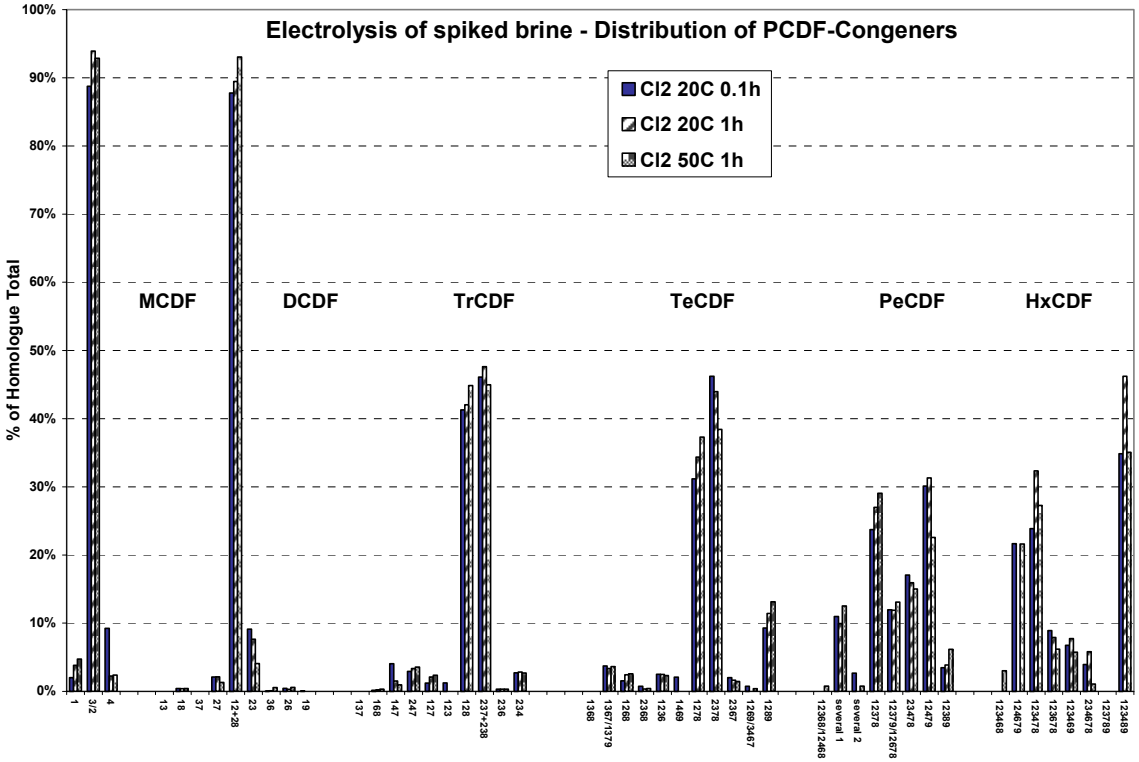
Figure 1: Comparison of the PCDF homologue totals in all experiments



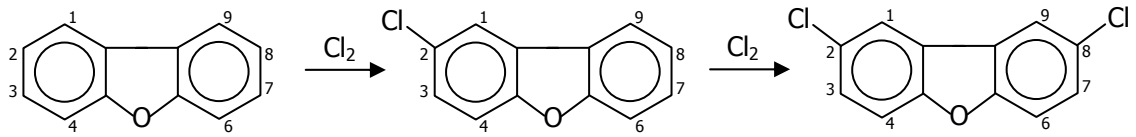
Comparing the results it is obvious that an extended electrolysis time seems to shift the distribution of the formed PCDF more towards the higher chlorinated homologues and that the conversion of the DBF to PCDF is clearly increased. A temperature increase with the same electrolysis time in both experiments leads only to minor differences with a slight shift also towards the higher chlorinated groups

In order to understand the formation mechanism the analysis included also the determination of all congeners from Mono- through OctaCDF.
The distribution of all detected congeners in all experiments is shown in Figure 2.
While the homologue totals show some differences in the experiments the distribution of the congeners is nearly identical under all experimental conditions with variation of electrolysis time and temperature.
This leads to the hypothesis that the formation of the PCDFs follows a distinct mechanism and that the reaction time and temperature has an impact only on the degree of chlorination but not on the formed congeners.
The mechanism of the chlorination of Dibenzofuran can be described as follows:

Figure 2: Distribution of the PCDF congeners in all experiments

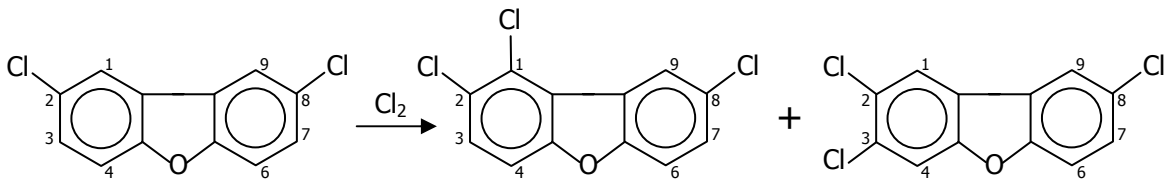


The oxygen in the DBF directs the electrophilic substitution to the ortho- and para-position favoring the para-positions which are 2 and 8. Therefore 2-MCDF (which is identical to the 8-position) is the major product of the monochlorination of DBF. Also in the further chlorination of 2-MCDF the p-direction of the oxygen is more favorable than the o/p-direction of the chlorine, resulting in the formation of mainly 28-DCDF, while 12-DCDF and 23-DCDF are only minor products.



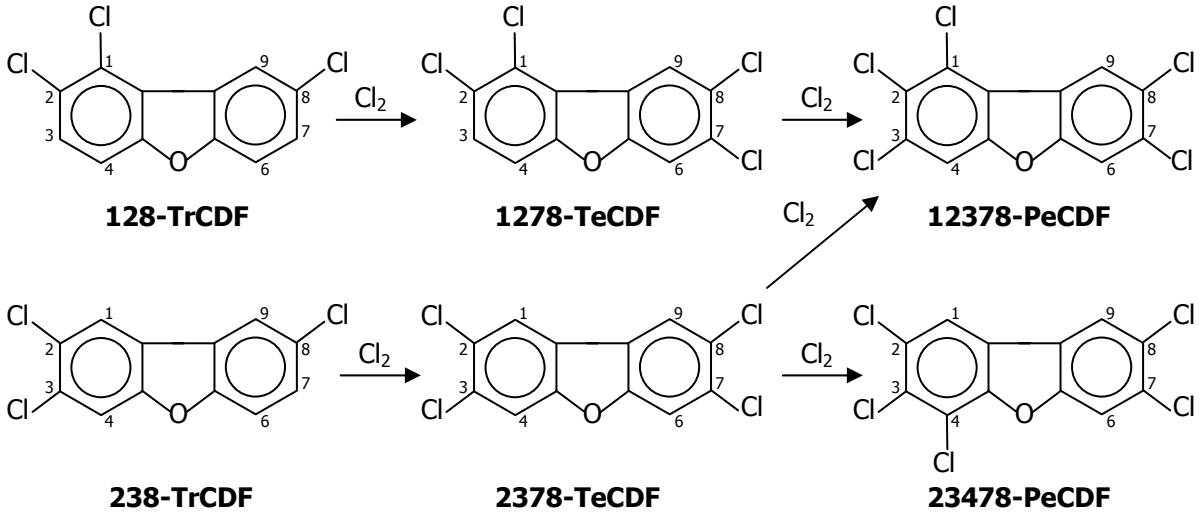
DBF **2-MCDF** **28-DCDF**

A continuous chlorination of 28-DCDF leads to 2 products, both a result of the ortho-direction of the chlorine: 128-TrCDF and 238-TrCDF.



28-DCDF **128-TrCDF** **238-TrCDF**

The introduction of another chlorine into these molecules favors the 7-position (ortho-position to the 8-chlorine and less hindered than for the other Cl-positions), resulting in the formation of 1278-TCDF and 2378-TCDF as the overall dominating components within this homologue group.
A further chlorination to PeCDF is apparently more impacted by sterical factors but still 12378-PeCDF (formed from both 1278- and 2378-TeCDF!) and 23478-PeCDF (from 2378-TeCDF only) are major products.



The chlorination of these congeners leads also only to 2378-substitued HxCDF-congeners. Other HxCDF are the result of the chlorination of non-2378-substituted PeCDF which derive from the minor-product route.

The main reaction pathway for the major products can be summarized as

DBF → 2-MCDF → 28-DCDF → 128-TriCDF → 1278-TeCDF → 12378-PeCDF
DBF → 2-MCDF → 28-DCDF → 278-TriCDF → 2378-TeCDF → 12378-PeCDF + 23478-PeCDF

12378-PeCDF → 123478-HxCDF + 123678-HxCDF + 123789-HxCDF
23478-PeCDF → 123478-HxCDF + 123678-HxCDF + 234678-HxCDF

This reaction pathway explains that chloroalkali electrolysis related PCDF with DBF as the source do have a unique pattern with the dominance of the 2378-substituted components. It also explains why an extension of the electrolysis time does lead to a shift to the more halogenated components but not to any change in the congener distribution.

Acknowledgements

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