

Formation studies of PCDD's and PCDF's using stable isotopes (^{18}O and ^{13}C)

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1. Abstract.

The formation of PCDD's and PCDF's on fly ash and a model fly ash is studied with activated carbon on flyash with $^{18}\text{O}_2$ and also from benzene ($^{12}\text{C}_6 + ^{13}\text{C}_6$) on alumina or silicagel with CuCl_2 or FeCl_3 as a catalyst.

During the $^{18}\text{O}_2$ experiment PCDD's and PCDF's were formed with an ^{18}O percentage ranging from less than 20 to more than 80 percent.

From a mixture of equal amounts of ^{12}C and ^{13}C benzene, PCDD's and PCDF's were formed. Most of the rings contained either ^{12}C or ^{13}C atoms. Under some conditions some scrambling did occur, indicating that also formation took place from degradationproducts of benzene.

Experiments with benzene as a precursor and CuCl_2 as a catalyst failed to give PCDD's and PCDF's under conditions where other precursors gave these compounds.

2. Introduction.

Although it is known now for many years that chlorinated dioxins and chlorinated dibenzofurans are formed in a municipal waste incinerator ¹⁾ little is known about the processes which take place during the formation of these compounds.

One of the controversies is whether small molecules are the precursors or macro molecules like activated carbon and PAH's.

In model experiments with graphite as a precursor no PCDD/F's are formed while activated charcoal or polycyclic aromatic compounds produced PCDD/F's with a congenerdistribution which is comparable with the pattern which is found in fly ash or the emissions of a MWI.

Experiments with chlorinated phenols as precursors gave a congener or isomer distribution which is completely different from what is found during normal incineration. The difference is so marked that often the terms "chloro-phenol" pattern and "incineration" pattern are used.

Although oxygen must play a role in the process little is known about the orrigin of this element during the reaction. To find out whether the oxygen from the air or the oxygen already present in the activated carbon is used, experiments were done with $^{18}\text{O}_2$.

Benzene has been used as a precursor compound in model experiments for formation of PCDD/F's. In these experiments PCDD's as well as PCDF's are formed. The PCDD formation can be explained by the oxydation and chlorination of benzene to chlorinated phenols and the subsequent condensation of these phenols to PCDD's. The mechanism of the formation of

PCDF's is not clear. The possibility of degradation of benzene to smaller fragments which rearrange to larger molecules could not be excluded.

The behaviour of a 1:1 mixture of ^{12}C benzene and ^{13}C benzene during model experiments could prove whether or not the benzene rings are broken during the reaction. The M^+ clusters of the mass spectra of the formed compounds is indicative for this. Not only the PCDD's and PCDF's formed can be studied in this way but also the intermediate compounds as there are the chlorinated benzenes and chlorinated phenols. Also the isomer and congener pattern of the formed PCDD/F's can be studied.

3. Experimental.

Experiments with $^{18}\text{O}_2$.

A mixture of 88.1% fly ash, 4.8% activated carbon, 5.0% NaCl and 2.1% CuCl_2 was heated in a glass tube in a heating-furnace at 366°C . A gas stream of 100 ± 2 mL/min N_2 was passed over the fly ash bed for 60 minutes to remove any present $^{16}\text{O}_2$. Subsequently a stream of 7.1 ± 1.1 mL/min. 90.0% N_2 , 9.7% $^{18}\text{O}_2$ and 0.3% $^{16}\text{O}_2$ was passed over the fly ash bed for 75 min. PCDD/F's evaporating from the fly ash surface were collected in a cold trap (100 mL toluene cooled with ice). The fly ash fraction and the cold trap were combined before the beginning of the soxhlet extraction. A blank taken from the reaction mixture contained no significant amounts of PCDD/F's before the experiment. The extraction and cleanup of the samples is described before ²⁾. The detection of the compounds was performed by HRGLC (50m DB-5) and HRSIM on a Kratos Concept. With this method, which is a modification of normal selected ion monitoring, a scan over each peak is made. The intensity and the accurate mass of each peak in the molecular ion cluster are measured in this way.

Experiments with benzene.

a) Alumina was impregnated with a solution of KCl and CuCl_2 in methanol. The methanol was evaporated under a nitrogen stream at 50°C , 5 gram of this mixture was placed in a glass tube between two bulbs of glasswool. This tube was placed in an oven and heated for two hours at different temperatures. Benzene (a 1:1 mixture of ^{12}C and ^{13}C) is evaporated onto the matrix by passing technical air, which first passed through a washing bottle filled with water, through a heated roundbottom flask (50°C) filled with benzene. After the gas tube, all volatile organic compounds were collected in a washing bottle filled with hexane and cooled in ice. The alumina matrix is analysed for PCDD/F's and the bottle after the gas tube is analysed for chlorophenols and chlorobenzenes.

The sample was soxhlet-extracted with toluene. The extract was purified and the PCDD/F's were identified with GC-MSD as described before ³⁾.

b) Method a) was modified so that FeCl_3 was used in stead of CuCl_2 and silicagel in stead of alumina. The temperatures used were around 400°C as described by ⁴⁾.

Extraction of the sample, cleanup and identification was identical with method a).

4. Results.

In table I the results are given for the amount of ^{18}O which is incorporated in the dibenzofuran molecules. The amounts vary from as low as 17% for 1,2,7,8-TCDF to more than 80% for the hepta chlorodibenzofurans.

Compound	% ¹⁸ O
TCDF	
1,3,6,8	49
1,4,6,8	25
1,2,4,7 / 1,3,4,7 / 1,3,7,8 / 1,3,4,6 / 1,2,4,6	27
1,3,6,7 / 1,3,4,8 / 1,3,7,9 / 1,2,4,8	33
1,2,6,8 / 1,4,6,7 / 1,4,7,8	31
2,3,6,8	48
2,4,6,7 / 1,2,3,8 / 1,2,3,6 / 1,4,6,9 / 1,6,7,8 / 1,2,3,4	34
1,2,7,8	17
1,3,4,9 / 1,2,6,7	38
2,3,4,8 / 2,3,7,8 / 2,3,4,7 / 2,3,4,6 / 1,2,4,9 / 1,2,7,9	45
2,3,6,7	69
3,4,6,7 / 1,2,6,9 / 1,2,3,9	76
PCDF	
1,3,4,6,8 / 1,2,4,6,8	49
1,3,6,7,8	72
1,2,3,6,8 / 1,2,4,7,8 / 1,3,4,6,7 / 1,3,4,7,8 / 1,2,4,6,7	68
1,3,4,7,9 / 1,4,6,7,8	56
1,2,4,7,9 / 1,3,4,6,9	63
2,3,4,6,8 / 1,2,4,6,9 / 1,2,3,4,7 / 1,2,3,4,6	37
1,2,3,4,8	39
1,2,3,7,8	68
1,2,3,6,7	70
1,2,6,7,8 / 1,2,3,7,9	59
2,3,4,7,8 / 1,2,4,8,9 / 1,2,6,7,9 / 1,2,3,6,9	73
2,3,4,6,7	77
1,2,3,4,9	50
H₁CDF	
1,2,3,4,6,8	61
1,3,4,6,7,8 / 1,2,4,6,7,8 / 1,3,4,6,7,9	75
1,2,4,6,7,9	79
1,2,4,6,8,9	83
1,2,3,4,6,7 / 1,2,3,4,7,8	72
1,2,3,6,7,8	75
1,2,3,4,7,9	80
1,2,3,4,6,9 / 1,2,3,6,7,9	78
1,2,3,6,8,9 / 2,3,4,6,7,8	79
1,2,3,7,8,9 / 1,2,3,4,8,9	72
H_pCDF	
1,2,3,4,6,7,8	74
1,2,3,4,6,7,9	80
1,2,3,4,6,8,9	81
1,2,3,4,7,8,9	84

Table I: Results of the ¹⁸O₂ experiment for the chlorinated dibenzofurans.

The results for the chlorinated dioxins are even more complicated. Here we have the possibility that one or two ¹⁸Oxygen atoms are incorporated and also here we don't find a regular pattern as can be seen in Table II. The pattern of the congeners and isomers is identical with that of a fly ash sample from a MWI.

Compound	% ¹⁶ O ₂	% ¹⁸ O ¹⁶ O	% ¹⁸ O ₂
TCDD			
1,3,6,8	50	0	50
1,3,7,9	35	35	30
1,3,6,9	40	35	25
1,2,4,7 / 1,2,4,8 / 1,3,7,8 / 1,4,6,9	40	20	40
1,2,4,6 / 1,2,4,9 / 1,2,6,8 / 1,4,7,8	55	30	15
1,2,7,9	40	20	40
1,2,3,4 / 1,2,3,6 / 1,2,6,9 / 1,2,3,7 / 1,2,3,8	65	10	25
2,3,7,8 / 1,2,3,9	30	30	40
1,2,7,8	45	25	30
1,2,6,7	70	5	25
PCDD			
1,2,4,6,8 / 1,2,4,7,9	15	20	65
1,2,4,6,9	25	25	50
1,2,3,6,8	10	30	60
1,2,4,7,8	10	25	65
1,2,3,7,9	10	25	65
1,2,3,6,9	15	35	50
1,2,4,6,7 / 1,2,4,8,9	20	25	55
1,2,3,4,7 interference			
1,2,3,4,6	55	5	40
1,2,3,7,8	10	20	70
1,2,3,6,7	15	25	60
1,2,3,8,9	15	25	60
H_iCDD			
1,2,4,6,7,9 / 1,2,3,6,8,9	15	5	80
1,2,3,4,6,8	10	25	65
1,2,3,6,7,9 / 1,2,3,6,8,9	5	25	70
1,2,3,4,6,9	20	20	60
1,2,3,4,7,8	10	20	70
1,2,3,6,7,8	10	20	70
1,2,3,4,6,7 / 1,2,3,7,8,9	10	20	70
H_pCDD			
1,2,3,4,6,7,9	5	25	70
1,2,3,4,6,7,8	5	25	70
OCDD			
1,2,3,4,6,7,8,9	5	20	75

Table II: Results of the ¹⁸O₂ experiment for the chlorinated dibenzo-p-dioxins.

As a result of the experiments with the benzene mixture and CuCl₂ as the catalyst chlorinated

dioxins and dibenzofurans were found after the reaction but only PCDD/F's with ^{12}C atoms were found. The chlorinated benzenes and chlorinated phenols which were found did contain either ^{13}C or ^{12}C rings, no mixing was observed. We repeated the experiments with another batch of normal benzene and after these experiments no PCDD/F's were found.

After the experiments with FeCl_3 as a catalyst ^{13}C , ^{12}C and mixed PCDD/F's were found. No or very little scrambling was found. The tetra-chlorinated compounds were formed in much higher amounts than the higher chlorinated PCDD/F's. The isomer pattern was a so called phenol pattern with the 1368 and 1379 TCDD as the main compounds. Chlorinated benzenes and chlorinated phenols were also found. No scrambling was detected and the lower chlorinated compounds were formed in much larger quantities than the higher chlorinated ones.

5. Conclusions

From the experiments with activated carbon and ^{18}O oxygen it is clear that the formation route is not the same for all the compounds. Only for the higher chlorinated compounds it is possible that a common reaction route exists and here dechlorination from higher chlorinated compounds to lower chlorinated compounds or chlorination from lower to higher chlorinated PCDD/F's is a possible explanation for the constant pattern of isomers which is found in fly ash and flue gas of municipal waste incinerators.

In general the higher chlorinated PCDD/F's are formed with the added oxygen and the lower chlorinated PCDD/F's are formed to a large extent by the use of bonden oxygen which is already present in the matrix. There are exceptions because the last eluting TCDF's use a relatively large amount of the added oxygen.

When the formation of polychlorinated dibenzo-p-dioxins from fragments with ^{18}O oxygen and fragments with ^{16}O oxygen is at random, one can predict the distribution. This predicted distribution does not fit with the experimental distribution. When the % of $^{18}\text{O}_2$ is around 70 as it is for the hexa-, hepta- and octaCDD, one expects values of 27 and 3% for the other contributions. The contribution of the mixed compound is to low and the contribution of the $^{16}\text{O}_2$ is to high. This is also found for the compounds where higher amounts of ^{16}O oxygen are incorporated.

There is a tendency that fragments with ^{16}O oxygen react with each other and this is also the case for fragments formed with ^{18}O oxygen.

It is very unlikely that fragments in the precursor matrix can move better than the oxygen molecules which are added during the reaction. This leads to the conclusion that in the carbon matrix dioxin-like structures are already present and that a large part of the PCDD/F's, and that is especially true for the lower chlorinated PCDD/F's are formed by the chlorination of these dioxin-like fragments.

From the experiments with benzene it can be concluded that formation of PCDD/F's with CuCl_2 does not take place and the formation which is found after experiments with benzene as a precursor is due to impurities in the benzene.

From the different results with two batches of benzene it can be concluded that there is a large difference in activity between different precursors.

It is possible to form PCDD/F's from benzene with FeCl_3 as a catalyst but the optimum temperature is much higher than with the normal PCDD/F formation with copper as a catalyst. Also the pattern of the compounds formed is not an incineration pattern but a chlorophenol pattern.

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6. References

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