

An Investigation of the Mechanism of Formation of Tetrachlorinated Dibenzo-p-dioxin and Tetrachlorinated Dibenzofuran in the Paper Pulp Industry.

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Abstract

Dibenzofuran (DF) and dibenzo-p-dioxin (DD), potential precursors in the formation of polychlorinated dibenzofuran (PCDF) and polychlorinated dibenzo-p-dioxin (PCDD), were chlorinated in an aqueous medium. The reaction products were analyzed for PCDD and PCDF. The typical pulp effluent isomer pattern is dominated by 2378-TCDF, 1278-TCDF and 2378-TCDD. Dominant reaction products observed were dichloro and trichloro congeners for the room temperature reactions, and trichloro congeners for the 80° reactions. It appears that the 2378-tetra substituted isomer is the most abundant among the tetrachloro congeners produced.

Introduction

The presence of PCDD and PCDF among the chlorinated compounds observed in paper pulp mill effluents was confirmed in 1986 [1]. Research efforts and government controls have resulted in reductions of PCDDs and PCDFs in pulp and effluents from the pulp and paper industry (PPI) since their discovery. However, little is known about the mechanism of formation of these compounds.

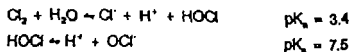
The objectives of the study are as follows: a) to gain more information regarding potential precursors of dioxins and furans in the PPI; b) acquire information regarding the mechanism of dioxin formation in the bleaching process of the PPI which will allow more efficient research and development on the inhibition and elimination of dioxin formation. In this investigation potential precursor compounds have been chlorinated in an aqueous medium. The products were analyzed for chlorinated dioxins and furans.

Background

Paper pulp is made from cellulose based materials, primarily hard and soft woods. The wood stock is chipped, mechanically or chemically pulped, chemically bleached, and finally converted into paper. The pulping and bleaching steps are designed to selectively remove lignin (a highly complex aromatic polymer) from the cellulose.

Kringstad, et al. [2] have concluded that dioxin formation must take place in the first chlorination step of the pulp bleaching sequence. Chlorination reactions with aromatic lignin fragments may lead to the formation of dioxins. However, according to Voss, et al. [3] non-chlorinated dibenzofuran (DF) is believed to be a major precursor for PCDF in pulp and paper mill effluents. Their investigation showed DBF as a contaminant in oil based defoaming solutions, as well as a ubiquitous contaminant in air, water, and possibly the original woodstock. Citing a paper by Gray and Dipinto [4], Voss indicates that the typical PCDF isomer pattern found in pulp and paper mill effluents is similar to that produced by direct, non-aqueous chlorination of DF (i.e. 2378-TCDF dominates, about half as much 1278-TCDF, trichloro-CDF, and minor amounts of other tetra and penta isomers). de Sousa, et al. [5] report that the 2378-TCDF and 2378-TCDD isomers are present in the highest concentrations.

Larson and Marley [6] studied the aqueous chlorination of terpenes which produces toxaphene-like compounds found in bleach plant effluents. The behaviour of chlorine in water is described:



Experimental

Initial chlorination experiments were done using DF as the precursor and Cl_2 as the chlorinating agent. An aqueous chlorination procedure described by Larson and Marley was used for all chlorinations using NaOCl as the chlorinating agent [6]. The experimental conditions are summarized in Table I.

Reaction flasks were wrapped in tinfoil during chlorination in an attempt to minimize the formation of Cl^- free radicals through exposure of Cl_2 to UV radiation.

Safety precautions were taken when using Cl_2 as the chlorinating agent. An N_2 purge line allowed excess Cl_2 gas to be flushed through the regulator valves after a reaction was completed. Additionally, a ventilation line was directed from the reaction flask into a 1M NaOH solution to trap unreacted chlorine.

The aqueous chlorination solutions were extracted with toluene, dried with Na_2SO_4 , filtered through sintered glass crucibles, and then reduced to 2.0 mL or less. All extracts were analyzed on an HP 5880 GC with ECD, using a 0.32 mm x 30 m DB-5 column (J & W Scientific), and an HP 5970 GC-MSD, using a 0.25 mm x 30 m DB-5 column (J & W Scientific).

Results and Discussion

Qualitative results from the GC-ECD analyses showed the majority of the chlorination products eluting in the same retention window as tetra- and pentachlorinated dioxins and furans (comparison with PCDD/PCDD*/PCDF lab standard) [Figure 1].

The main chlorination products observed in the total ion chromatograms (GC-MSD linear scans) were identified from their mass spectra as mono, di, tri, and sometimes tetra chlorinated congeners of DBF or DBD. GC-MS electron impact selected ion monitoring (EISIM) was used to confirm the identification [Figure 2], and quantitation. Quantitative results are summarized in Table II. 2378-TCDF was tentatively identified in the DBF/H ECD traces. 2378-TCDF and 2378-TCDD were identified in GC-MS EISIM runs [Figure 3].

The qualitative and quantitative GC-MSD results show that the dichloro and trichloro congeners are the most prevalent of the PCDD and PCDF compounds formed in the room temperature reactions. Temperature and time variations do not appear to be sufficient to drive the chlorination reaction beyond the tetra substituted stage.

Conclusions

The typical bleached pulp PCDD/PCDF isomer pattern has not been observed in the aqueous chlorination experiments of DD and DF as described above. If DD and DF are indeed major precursors of PCDD and PCDF in bleached pulp and pulp and paper mill effluent, other factors such as possible catalytic effects from metal ions may be responsible to form 2378-TCDD/TCDF as the major dioxin products. Temperature and time factors, more rigorous than those found in mill bleaching operations, are not sufficient to drive the chlorination beyond tetra-substituted congeners. Of the tetrachloro- congeners produced, it appears that the most abundant isomers are 2378-substituted.

References

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Table I. Summary of experimental conditions.

No.	Precursor	mass (mg)	Solvent	vol (mL)	Cl ₂ Source	Temp (°C)	Time
A. DBF/Cl₂							
1		50		100		65	5m
2	DBF	40	20%	200	Cl _{2(gas)}	80	5m
3		40	EtOH/H ₂ O	200		80	30m
4		40		200		80	90m
B. DBF/H*							
1		40		100		rt	90m
2	DBF	40	1M HCl	100	NaOCl	rt	4h
3		40		100	(20mL)	rt	23h
4		40		100		80	23h
C. DBF/C							
1	DBF	40	1M HCl	100	Cl _{2(gas)}	80	6h
D. DBD/H							
1		1.0		10		rt	
2	DBD	1.0	1M HCl	10	NaOCl	rt	6h
3		1.0		10	(10mL)	80	
4	+FeCl ₃ (0.1g)	1.0		10		rt	
5	+Cu (1.4g)	1.0		10		rt	
E. DBF/H							
1		1.1		10		rt	
2	DBF	1.1	1M HCl	10	NaOCl	rt	6h
3		1.1		10	(10mL)	80	
4		1.1		10		80	

Table II. Summary of quantitation results.

Sample I.D.	D ₂ CDD		I ₂ CDD		I ₁ CDD		Total
D. DBD/H	(µg)	(%)	(µg)	(%)	(µg)	(%)	(% rec)
1	440	32	160	10	40	2	44
2	390	29	220	14	44	3	46
3	28	2	410	27	190	11	40
E. DBF/H	D ₂ CDF		I ₂ CDF		I ₁ CDF		Total
	(µg)	(%)	(µg)	(%)	(µg)	(%)	(% rec)
1	300	20	290	16	89	5	41
2	170	11	250	14	70	4	29
3	110	7	890	51	190	10	68
4	150	10	760	43	130	7	60
B. 2	140	24	130	20	220	3	47

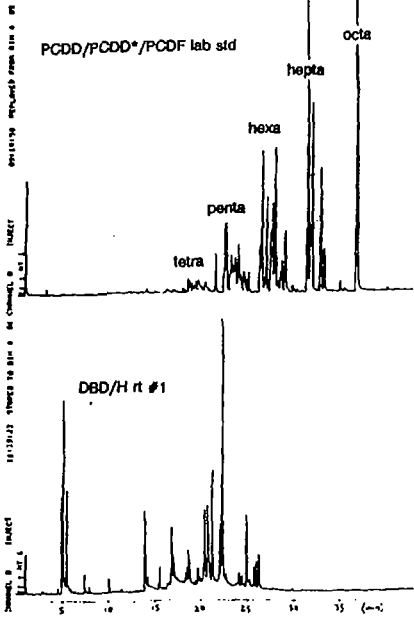


Figure 1. Comparison of ECD traces of PCDD/PCDD*/PCDF lab standard with DBD/H.

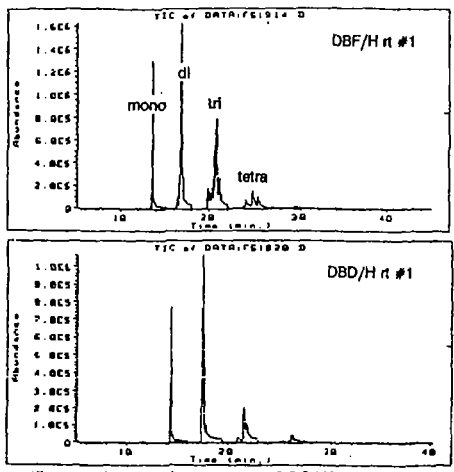


Figure 2. Total ion chromatogram of GC-MSD SIM run.

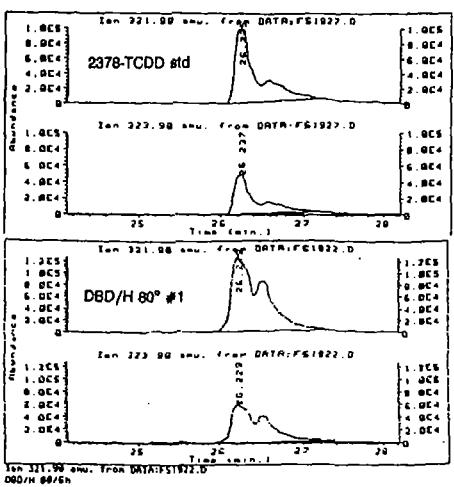


Figure 3. Ion traces of M^{2+} and M^{14+} ions of 2378-TCDD std and DBD/H sample.