



Project Summary

Dioxin and Furan Contamination in the Manufacture of Halogenated Organic Chemicals

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The manufacture of halogenated organic chemicals results in the formation of small amounts of undesirable side reaction by-products. These contaminants may be contained in the product chemical, separated into a processing step residue, or lost to the air or wastewater as a pollutant. The halogenated dibenzo-p-dioxins (dioxins) and halogenated dibenzofurans (furans) are substances which may be hazardous to human health or the environment. Identification of sources of these compounds will aid strategies to protect the public from exposure to these chemicals.

For several years, attention has been focused on one member of the dioxin family, namely 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). In this report, a brief review of important chlorinated organic chemicals associated with dioxin and furan contamination is followed by an extensive discussion of brominated organic chemical manufacturing. Potential for dioxin and furan contamination is predicted and available information on actual product analysis is presented. The results of this study may be used to identify sources of dioxins and furans and to develop methods to eliminate, reduce or isolate the occurrence of these compounds.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same

title (see Project Report ordering information at back).

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) have been the subject of intensive study by the scientific community for many years. Often dubbed as the "most toxic man-made substances," "carcinogenic," etc., the health and environmental risks of this class of chemicals are a major concern throughout the world.

There has been much confusion as to when PCDDs and their toxic effects first became known to the scientific world. The composition and toxic effects of PCDDs were known and reported in the scientific literature as early as 1957.

Polychlorinated dibenzofurans (PCDFs) are another class of contaminants that have aroused public concern. They are frequently found with PCDDs in chlorophenol products and also as contaminants in polychlorinated biphenyls (PCBs). Fires involving PCB-filled transformers and capacitors have been found to generate relatively large amounts of PCDFs.

The U.S. Environmental Protection Agency has taken a number of regulatory actions to control these substances. Actions by the Office of Pesticide Programs have effectively banned the use of trichlorophenol-based pesticide substances such as 2,4,5-T and Silvex® in which the contaminant 2,3,7,8-TCDD has been found. Recently, the Office of Solid Waste and Emergency Response, acting under the Resource

Conservation and Recovery Act (RCRA), has proposed new rules for PCDDs- and PCDFs-contaminated wastes specifying stringent waste treatment requirements. Additional action has also been taken to control exposure to PCBs. Concern over the generation of PCDFs and PCDDs in PCB-containing transformer fires has led to new regulations by the Office of Toxic Substances for phased removal and replacement of the PCB transformers.

To date, scientific and regulatory interests have focused primarily on chlorinated substances, in particular the PCDDs, of which the 2,3,7,8-tetrachloro isomer has been the subject of greatest study. Similar chemical reactions are known to occur in the manufacture of brominated chemicals and thus polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofuran (PBDFs) may be formed as undesired contaminants in certain brominated chemical substances.

The full report presents available data on processes used in the manufacture of brominated compounds which are most likely to be contaminated with PBDDs and PBDFs. The chemical reactions involved in the synthesis of the brominated compounds are evaluated in light of the reaction mechanisms that lead to the formation of polyhalogenated dioxins and furans. Through this assessment, it may then be possible to identify critical data gaps and needs, such as product assays and process modifications to reduce the release of PBDDs and PBDFs into the environment.

Brominated Organic Chemicals

Table 1 gives basic information on brominated organic chemicals which have a potential for PBDD or PBDF contamination due to the raw materials and processes used in their manufacture. Relatively little recent data are available due to the confidential nature of business information in the organic chemicals industry.

Few brominated organic chemical products have undergone chemical analysis for the presence and concentration of dioxin and furan contamination. Some information is available for 2,4,6-tribromophenol, pentabromophenol and tetrabromobisphenol A. The analytical procedure in each case was high resolution gas chromatography/mass spectrometry. No dioxins or furans were found in the pentabromophenol.

Contaminants in the 2,4,6-tribromophenol included:

- Dibromodibenzo-p-dioxin
- Tribromodibenzo-p-dioxin
- Tetrabromodibenzo-p-dioxin (main component, ~90 ppb)
- Pentabromodibenzo-p-dioxin
- Dibromodibenzofuran
- Tribromodibenzofuran
- Tetrabromodibenzofuran
- Pentabromodibenzofuran
- Hexabromodibenzofuran
- Heptabromodibenzofuran
- Octabromodibenzofuran

Contaminants in the tetrabromobisphenol A were:

- Pentabromodibenzofuran
- Hexabromodibenzofuran
- Heptabromodibenzofuran
- Octabromodibenzofuran (main component, ~30 ppb)

Possible reaction pathways and most likely dioxin and furan contaminants are listed for many other compounds appearing in Table 1.

Table 1. Compounds with Potential PBDD and PBDF Contamination

Name	Structure	Uses	Production
BROMINATED PHENOLS			
4-Bromo-2,5-dichlorophenol - 2,5-Dichloro-4-bromophenol - Leptophos phenol - Phosvel phenol		N.D.	N.D. ¹
o-Bromophenol - 2-Bromophenol		- Synthesis of resorcinol, other organics	N.D.
m-Bromophenol - 3-Bromophenol			N.D.
p-Bromophenol - 4-Bromophenol		- Antiseptic - Synthesis of other compounds	N.D.
2,6-Dibromo-4-nitrophenol - 4-Nitro-2,6-dibromophenol			≥5,000 lbs or \$5,000 sales (USITC, 1984)
2,4-Dibromophenol		- Flame retardant intermediate	N.D.
2,6-Dibromophenol		N.D.	<1,000 lbs/yr (EPA estimate)
Pentabromophenol - Flammex 5BP		- Flame retardant intermediate - Molluscicide (experimental)	N.D.
Tetrabromocatechol - Tetrabromopyrocatechol		N.D.	N.D.
2,4,6-Tribromo-m-cresol - 2,4,6-Tribromo-3-methylphenol - Triphysan - Triphysol		N.D.	N.D.
2,4,6-Tribromophenol - Bromkal Pur 3 - Bromol - Flammex 3BP - Great Lakes PH-73 - Tribromophenol		- Flame retardant intermediate - Anti-fungal agent - Chemical intermediate - Antiseptic germicide	≥2.27 × 10 ³ kg (1979) ≥4.54 × 10 ³ kg (1981)

Table 1. (Continued)



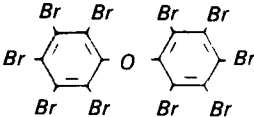
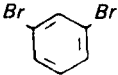
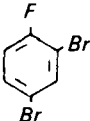
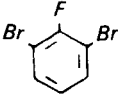
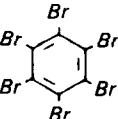
Name	Structure	Uses	Production
BROMINATED COMPOUNDS			
Bromobenzene - Monobromobenzene - Phenylbromide		- Solvent - Top-cylinder compound - Chemical intermediate	≥ 454 kg (1972) ≥ 450 kg (1975) $\geq 5,000$ lbs or $\geq \$5,000$ sales (USITC, 1981)
o-Bromofluorobenzene - 1-Bromo-2-fluorobenzene - o-Fluorobromobenzene - 2-Fluorobromobenzene - 1-Fluoro-2-bromobenzene			$< 1,000$ lbs/yr (EPA CBI Aggregate)
Decabromodiphenyloxide - Berkflam B10E - Bis (pentabromophenyl) ether - Bromkal 81 - Bromkal 82-ODE - Bromkal 83-1ODE - BR55N - DE 83 - DE 83R - Decabrom - Decabromobiphenyl ether - Decabromobiphenyloxide - Decabromodiphenyl ether - Decabromophenoxybenzene - Decabromophenyl ether - EB10FP - EBR 700 - FR 300 - FR 300BA - FRP 53 - FR-PE - Planelon DB100 - Saytex 102 - Saytex 102E		- Flame retardant	$2-8$ million lbs yr (1976)
2,6-Dibromobenzene - m-Dibromobenzene - 1,3-Dibromobenzene		- Ingredient of fire extinguishers - Flame retardant - Ingredient of heat transfer fluids	N.D.
2,4-Dibromofluorobenzene - 1,3-Dibromo-4-fluorobenzene		- Intermediate for agricultural and pharmaceutical chemicals	N.D.
2,6-Dibromofluorobenzene		N.D.	N.D.
Hexabromobenzene - Benzene hexabromide - HBB - Perbromobenzene		- Flame retardant	≥ 908 kg (1972) ≥ 454 kg (1975)

Table 1. (Continued)

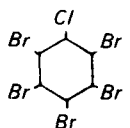
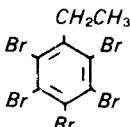
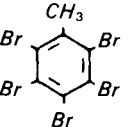
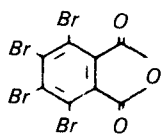
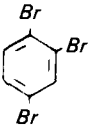
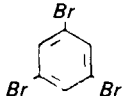
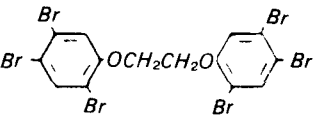
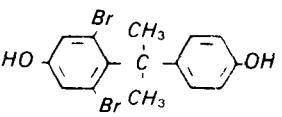
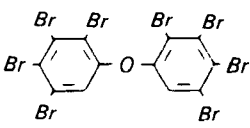
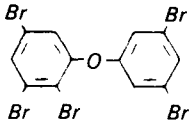
Name	Structure	Uses	Production
Pentabromochlorocyclohexane - Chloropentabromocyclohexane - FR 651A - 1,2,3,4,5-Pentabromo-6-chlorocyclohexane		- Flame retardant	10 ⁶ -10 ⁷ lbs/yr (EPA estimate)
Pentabromoethylbenzene - EB 80 - Saytex 105		- Flame retardant	N.D.
Pentabromotoluene - Flammex 5BT - Pentabromomethylbenzene		- Flame retardant	N.D.
Tetrabromophthalic Anhydride - Bromphthal - FG 4000 - FireMaster PHT4 - Great Lakes PHT4 - Saytex RB-49		- Flame retardant	$\cong 2.27 \times 10^3$ kg (1979) $\cong 6.81 \times 10^3$ kg (1981)
1,2,4-Tribromobenzene		- Oil additive	N.D.
1,3,5-Tribromobenzene		- Oil additive	N.D.
BROMINATED BISPHENOLS			
1,2-Bis(tribromophenoxy) ethane - BTBPE - FireMaster 680		- Flame retardant	N.D.
2,6-Dibromobisphenol A		- Flame retardant	N.D.
Octabromodiphenyl oxide - DE-79 - FR 143 - Octabromodiphenyl ether - 1,1'-Oxybis-octabromobenzene - Tardex 80		- Flame retardant	N.D.
Pentabromodiphenyl oxide - DE71 - 1,1'-Oxybis-pentabromobenzene - Pentabromodiphenyl ether		- Flame retardant	N.D.

Table 1. (Continued)

Name	Structure	Uses	Production
<p>Tetrabromobisphenol A</p> <ul style="list-style-type: none"> - BA 59 - BA 59P - 2,2-Bis(3,5-dibromo-4-hydroxyphenyl) propane - Bromdian - Fireguard 2000 - FireMaster BP4A - 4,4'-Isopropylidene bis-(2,6-dibromophenol) - Saytex RB-100 - Tetrabrodian - Tetrabromodihydroxy diphenyl propane 		<ul style="list-style-type: none"> - Flame retardant - Plasticizer (limited) 	> 10 ⁶ lbs/yr
<p>Tetrabromobisphenol A, allyl ether</p> <ul style="list-style-type: none"> - 1,1-(1-Methylethylidene)-bis(3,5-dibromo)-4-(2-propenyloxy)-benzene 		<ul style="list-style-type: none"> - Flame retardant 	N.D.
<p>Tetrabromobisphenol A-bis-2,3-dibromopropyl ether</p> <ul style="list-style-type: none"> - 2,2-Bis[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]-propane - Fire Guard 3100 - Great Lakes PE-68 		<ul style="list-style-type: none"> - Flame retardant - Propane 	N.D.
<p>Tetrabromobisphenol A-bisethoxylate</p>		<ul style="list-style-type: none"> - Flame retardant 	N.D.
<p>Tetrabromobisphenol A, bismethylether</p>		<ul style="list-style-type: none"> - Flame retardant 	N.D.
<p>Tetrabromobisphenol A-diacrylate</p> <ul style="list-style-type: none"> - 4,4'-Isopropylidene-bis(2,6-dibromophenyl)-acrylate) 		<ul style="list-style-type: none"> - Flame retardant 	N.D.
<p>Tetrabromobisphenol B</p>		<ul style="list-style-type: none"> - Flame retardant 	N.D.
PESTICIDES			
<p>Bromophos</p> <ul style="list-style-type: none"> - Brofene - o-(4-Bromo-2,5-dichlorophenyl)-o,o-dimethyl, phosphorothioate - Bromofos - Brophene - Nexion - Nexion 40 - S1942 		<ul style="list-style-type: none"> - Insecticide 	N.D.

Table 1. (Continued)

Name	Structure	Uses	Production
Bromoxynil butyrate - 2,6-Dibromo-4-cyano-phenyl butanoic ester		- Insecticide	N.D.
Bromoxynil octanoate - Bronate - Buctril - 3,5-Dibromo-4-octanoyl-oxybenzotrile		- Herbicide	N.D.
Profenofos - o-(4-Bromo-2-chloro-phenyl)-o-ethyl-S-propyl-phosphorothioate - CGA 15324 - Curacron - Polycron - Selecron		- Insecticide	N.D.

¹N.D. = No Data

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Brian A. Westfall is the EPA Project Officer (see below).

The complete report, entitled "Dioxin and Furan Contamination in the Manufacture of Halogenated Organic Chemicals," (Order No. PB 87-119 905/AS; Cost: \$13.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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