HETEROCYCLES, Vol 28, No. 2, 1989

FORMATION OF HETEROCYCLIC HAZARDOUS COMPOUNDS BY THERMAL DEGRADATION OF ORGANIC COMPOUNDS

Dieter Bieniek, Müfit Bahadir, and Friedhelm Korte
Gesellschaft für Strahlen- und Umweltforschung mbH München, Institut für Ökologische Chemie, Ingolstädter Landstr. 1, D-8042 Neuherberg, F.R.G., and Technische Universität München, Institut für Chemie, Am Löwentor, D-8050 Freising-Weihenstephan, F.R.G.

Dedicated to Sir Derek Barton on the occasion of his 70th birthday

Abstract - 2,3,7,8-Tetrabromodibenzofuran in ppm concentrations can be generated via reductive debromination and subsequent intramolecular cyclization during thermolysis of polybrominated aromatic compounds such as decabromodiphenyl ethers which are used as flame retardants in plastics. The respective tetrabromodibenzodioxin isomer is produced in moderate amounts. In analogy to the chlorinated isomers the formation of toxic substances from incineration or fire accident constitutes a potential hazard.

Depending on the reaction conditions and on the components of the combustion material incomplete incineration processes result in the formation of numerous toxic or persistent organic compounds such as polycyclic aromatic hydrocarbons, or polycyclic aromatic compounds containing nitrogen, oxygen, sulfur, halogen, nitro, or cyano functional groups[1]. The generation of chlorinated and brominated dibenzodioxins and -furans during thermal processes is subject to intensive research because of the extreme toxicity of those compounds[2]. Numerous plastic products which are used in areas exposed to fire hazard contain flame retardants. Brominated aromatic compounds e.g. decabromodiphenyl ether, tetrabromobisphenol A or hexabromocyclododecane are important flame retardants.

The pyrolysis of pure 2,4,6-tribromophenol at 800°C in open quartz tubes gives rise to the formation of tetrabromodibenzodioxins (TBrDDs) with a yield of 89.6 %. The total conversion of polybrominated dibenzodioxins (PBrDDs) and dibenzofurans (PBrDFs) was 94.9 %.

Under identical conditions tetrabromobisphenol A yielded mainly mono- and dibromodioxins and -furans. The TBrDD and TBrDF isomers were produced at a concentration of 27 or 21 ppm, respectively[3]. Thermolysis of technical grade polybrominated diphenyl ether at 510-630°C resulted in PBrDDs and PBrDFs at total yields of up to 10 %[4].

Hexabromobenzene (5 %) is the main product formed from pure decabromodiphenyl ether. Pentabromobenzene (0.5 %), penta- and hexabromobenzofurans (0.1 %) as well as tetrabromoethene, hexabromobutadiene, tribromophenol and octabromostyrene are generated in low amounts. The concentration of those products decreases with increasing temperature of thermolysis.

In addition, investigations of the thermolysis of plastics containing flame retardants are important for the modeling of fire accidents as well as waste incineration. Therefore, our group investigated the influence of temperature and oxygen content of the combustion gas on the formation of PBrDD and PBrDF from plastics containing decabromodiphenyl ethers as flame retardants. So far, our results show that dibenzofurans with higher bromine content are formed by thermolysis of plastics containing decabromodiphenyl ether in the presence of antimony trioxide as synergist. At 400°C, approx. 4000 ppm tetrabromodibenzofuran (TBrDF) was detected. With increasing temperature the concentration of TBrDFs decreased below their detection limit at 800°C[5] (see Table 1). An oxygen content between 8-20 % (v/v) in air had no significant influence on the formation of these hazardous products. The synergist, antimony trioxide, played an important role on their formation. The reaction mechanisms are being investigated at present.

At 400°C 2,3,7,8-TBrDF and 2,3,7,8-TBrDD at concentrations of 0.1-4.5 ppm and 0.1-4.0 ppm, respectively, are formed from various other plastics containing decabromodiphenyl ether. With increasing temperature the concentration of those isomers decreases until they are no longer detectable at 800°C (detection limit: 0.01 ppm). The formation of PBrDF and PBrDD is outlined in the following reaction scheme.

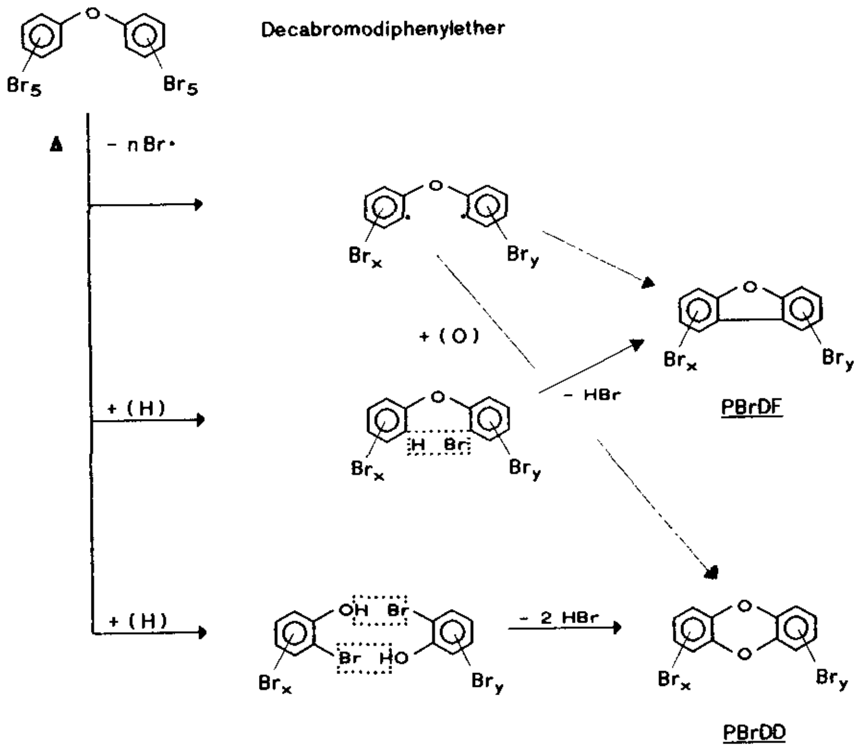
Table 1

Thermolysis products of polybutylene terephthalate with 10 % decabromodiphenyl ether and 6 % Sb_2O_3.

	Temperature in °C				
Bromodibenzofurans	400	500	600	700	800
Mono-	100	300	100	50	-
Di-	500	400	200	10	-
Tri-	3000	2000	400	-	-
Tetra-	4000	3000	600	-	-
Penta-	4000	1000	200	-	-
Hexa-	1000	200	-	-	-
Hepta-	500*	-	-	-	-

Semiquantitative values in ppm based on the material used

- = not detected; * = not exactly identified



PBrDF including the 2,3,7,8-tetrabromo isomer can be formed via elimination of Br_2 or HBr after reductive debromination followed by intramolecular cyclization. PBrDD is formed in intramolecular cyclization reactions during the attack of an oxygen radical on the diphenyl ether molecule or by cyclization of phenolic intermediates.

The identification and quantification of nano- and picogram concentrations of PBrDD/DF in complex matrices requires selective sample preparation. Various column packing materials (Florisil, aluminum oxide) were used for the liquid chromatographic isolation of PBrDD/DF from combustion products.

Interfering substances could be removed by selective adsorption on those materials followed by elution with hexane/dichloromethane mixtures. Recovery and efficiency of the analytical steps were controlled with standard substances. The use of ^{13}C-labelled standards in combination with mass spectrometry guarantee a high degree of analytical reliability. HRGC/MS-SIM was used for the final quantification.

REFERENCES

1. G. Politzki, E.S. Lahaniatis, and D. Bieniek, Chemosphere, 1984, 13, 191
2. H.-R. Buser, Chemosphere, 1987, 16, 713
3. H. Thoma, S. Rist, G. Hausschulz, and O. Hutzinger, Chemosphere, 1986, 15, 649
4. H.-R. Buser, Environ. Sci. Technol., 1986, 20, 404
5. E. Clausen, E.S. Lahaniatis, M. Bahadir, and D. Bieniek, Fresenius Z. Anal. Chem., 1987, 327, 297

Received, 26th September, 1988