

Formation of Brominated Dibenzofurans from the Photolysis of Flame Retardant Decabromobiphenyl Ether in Hexane Solution by UV and Sun Light

Isao Watanabe¹ and Ryo Tatsukawa²

¹Osaka Prefectural Institute of Public Health, Nakamichi 1-3-69, Higashinari-ku, Osaka 537 and ²Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama 790, Japan

Decabromobiphenyl ether (DBBE), a completely brominated congener in polybrominated biphenyl ethers (PBBEs), is used as a flame retardant in materials such as resins, textiles and paints. This compound, next to Tetrabromobisphenol-A [2,2'-bis(4-hydroxy-3,5-dibromophenyl)propane] is consumed most among brominated flame retardants in Japan. Its annual consumption has increased year by year and was about 2900 tons in 1984 in Japan.

Lower brominated biphenyl ethers such as tetrabromobiphenyl ethers (tetra-BBEs) and pentabromobiphenyl ether (penta-BBEs) are also used as flame retardants in Western Europe and USA and regarded as environmental pollutants due to their significant levels detected in fish in Sweden (Andersson and Blomkvist 1981). Substantial levels of DBBE have also been confirmed in river sediment collected from Osaka, Japan, as reported previously (Watanabe et al. 1986). This finding demonstrates DBBE to also be present as an environmental pollutant in Japan.

Recently, Buser (1986) reported the formation of polybrominated dibenzofurans (PBDFs) and dibenzo-p-dioxins (PBDDs) from the pyrolysis of PBBEs, indicating these hazardous compounds to possibly arise from the incineration or accidental burning of material containing PBBEs.

In addition to pyrolysis products, attention should also be directed to those of photolysis as a source of environmental pollutants. Polychlorinated biphenyl ethers (PCBEs) in an organic solvent give dechlorinated biphenyl ethers and chlorinated dibenzofurans as the major products on photolysis, as reported by Choudhry et al. (1977) and Mamantov (1985). Thus the formation of PBDFs by photolysis of PBBEs since their chemical structures are essentially the same as those of PCBEs.

In the present study, identification was made of PBDFs from the photolysis of the DBBE in hexane solution by ultraviolet (UV) and sun light.

Send reprint requests to I. Watanabe at the above address.

MATERIALS AND METHODS

The DBBE investigated in this work was a technical material produced by a chemical industrial company in Osaka, Japan. This substance contained a small amount, about 3%, of nonabrominated biphenyl ether as impurity. 2,3,7,8-Tetrabromodibenzofuran (2,3,7,8-tetra-BDF) as a qualitative reference compound was kindly provided by Dr. Andrew S. Kende (University of Rochester, NY, USA). All solvents used were of analytical grade.

A Varian 1800 gas chromatograph connected to an electron capture detector (^{63}Ni) was used to determine DBBE content in the photolysis samples of DBBE, under the following conditions: separation column, 2%OV-1 column (2mm x 1.0m); column temperature, 285C; carrier gas (N_2) flow rate, 40ml/min. A JEOL JMS DX-300 mass spectrometer connected to a Hewlet Packard 5710A gas chromatograph and a JEOL JMS 3500 data system were used to identify the photolysis products of DBBE, under the following conditions: separation column, a 25m OV-1 fused silica capillary column (0.32mm i.d., crosslinked, 0.25mm film thickness); column temperature, 150 - 320C(8C/min.); carrier gas (He) flow rate, 1.0ml/min., electron impact ionization voltage, 70 eV.

Semiquantitation of the photolysis products was also conducted by comparing the peak area of 4,4'-di-BBE obtained commercially, with those of the photoproducts on reconstructed ion chromatograms (M/Z=100 - 900). Response toward 4,4'-di-BBE and photoproducts of DBBE was assumed the equal on the reconstructed ion chromatograms.

100 $\mu\text{g/ml}$ of DBBE in a mixture of hexane, benzene and acetone (8:1:1) were prepared as a sample for photolysis. 50ml of this solution were introduced into a quartz tube (15mm x 30cm) followed by irradiation by UV, using a mercury lamp (254nm dominant) and sun light. After irradiation, 5ml aliquots were removed from the solution at specified times. The photoproducts present in each sample were analyzed directly by GC and GC-MS, as described above, for composition and presence of debrominated compounds and PBDfs.

RESULTS AND DISCUSSION

Figure 1 shows a reconstructed ion chromatogram (M/Z=100 - 900) of a sample irradiated for 16 hours by UV, using GC-MS. Debrominated compounds of DBBE, i.e., tri- to octabrominated congeners, were found to be the major products, as evident from the figure. Norris et al. (1973) reported DBBE dissolved in xylene to undergo photodegradation to lower brominated compounds by reductive debromination. This present data confirm this finding.

The formation of PBDfs as other major photoproducts of DBBE was also noted in the present study. Figure 2 shows the EI mass spectra of the 2,3,7,8-tetra-BDF standard and peaks of the main components of 1F, 2F, 3F, 4F, 5F and 6F appear in Figure 1. 2,3,7,8-Tetra-BDF has M^+ ions as base peaks and $(\text{M}-\text{Br})^+$, $(\text{M}-\text{COBr})^+$, $(\text{M}-\text{Br}_2)^+$, $(\text{M}-\text{COBr}_2)^+$, $(\text{M}-\text{COBr}_3)^+$ and $(\text{M}-\text{COBr}_4)^+$ as frag-

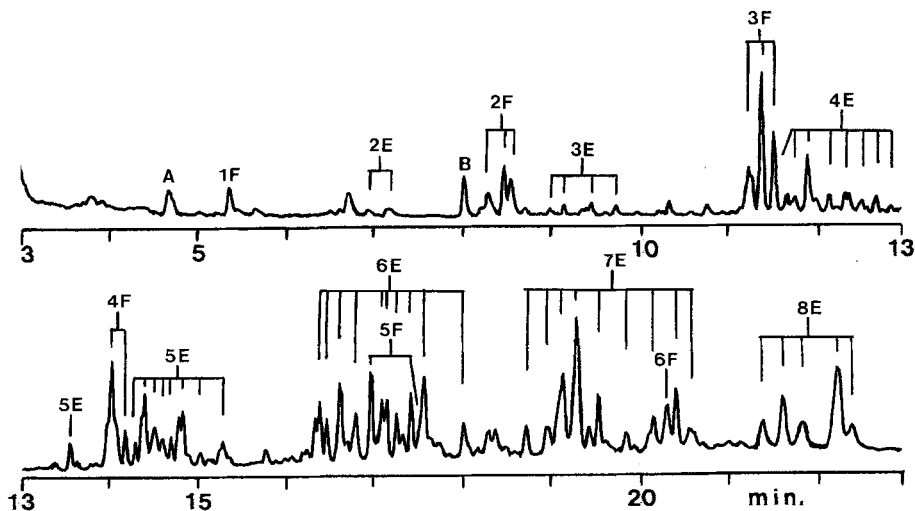


Figure 1. Reconstructed ion chromatogram ($M/Z=100-900$) of photoproducts of DBBE by UV for 16 hours. Peak identification: PBBEs as 4E (tetra-BBE), etc.; PBDFs as 4F (tetra-BDF), etc.; other peak assignments: A, tetrabromobenzen; B, pentabromobenzene.

ment ions, as described by Buser (1986) (Figure 2-a). $(M-COBr_4)^+$ ions were produced as a result of the complete removal of all bromine substituents and CO ($C_{11}H_{8-x}$, where x is the number of bromines of PBDFs). The mass spectrum of the main component peak of 4F in Figure 1 is the same as that of 2,3,7,8-tetra-BDF though the relative intensities of fragment ions differ somewhat in both. Buser (1986) reports that such differences could be observed for PBDF isomers in the relative fragment ion ratios, especially $(M-Br_2)^+/(M-COBr)^+$. Thus, the compound of the main component peak of 4F in Figure 1 was identified as a tetra-BDF but not 2,3,7,8-Tetra-BDF.

In consideration of the above, the compounds of the peaks 1F, 2F, 3F, 5F and 6F in Figure 1 were identified as mono-, di-, tri-, penta- and hexa-BDF, respectively, based on their M^+ ions and characteristic fragment ions. This indicates that hepta- and octa-BDF were not present in this sample.

Tetra- and pentabromobenzene were also found as minor photoproducts from DBBE by UV, as shown in Figure 1. However, the formation of PBDDs were recognized as pyrolysis products of PBBEs could not be detected.

Figure 3 shows schematically the formation and disappearance of PBBEs and PBDFs by the UV photolysis of DBBE. DBBE was photodegraded readily into lower brominated biphenyl ethers and PBDFs, as shown in this figure. The formation of PBDFs appeared to occur secondarily from debrominated biphenyl ethers as photoproducts of DBBE, but not directly from DBBE, as evident from

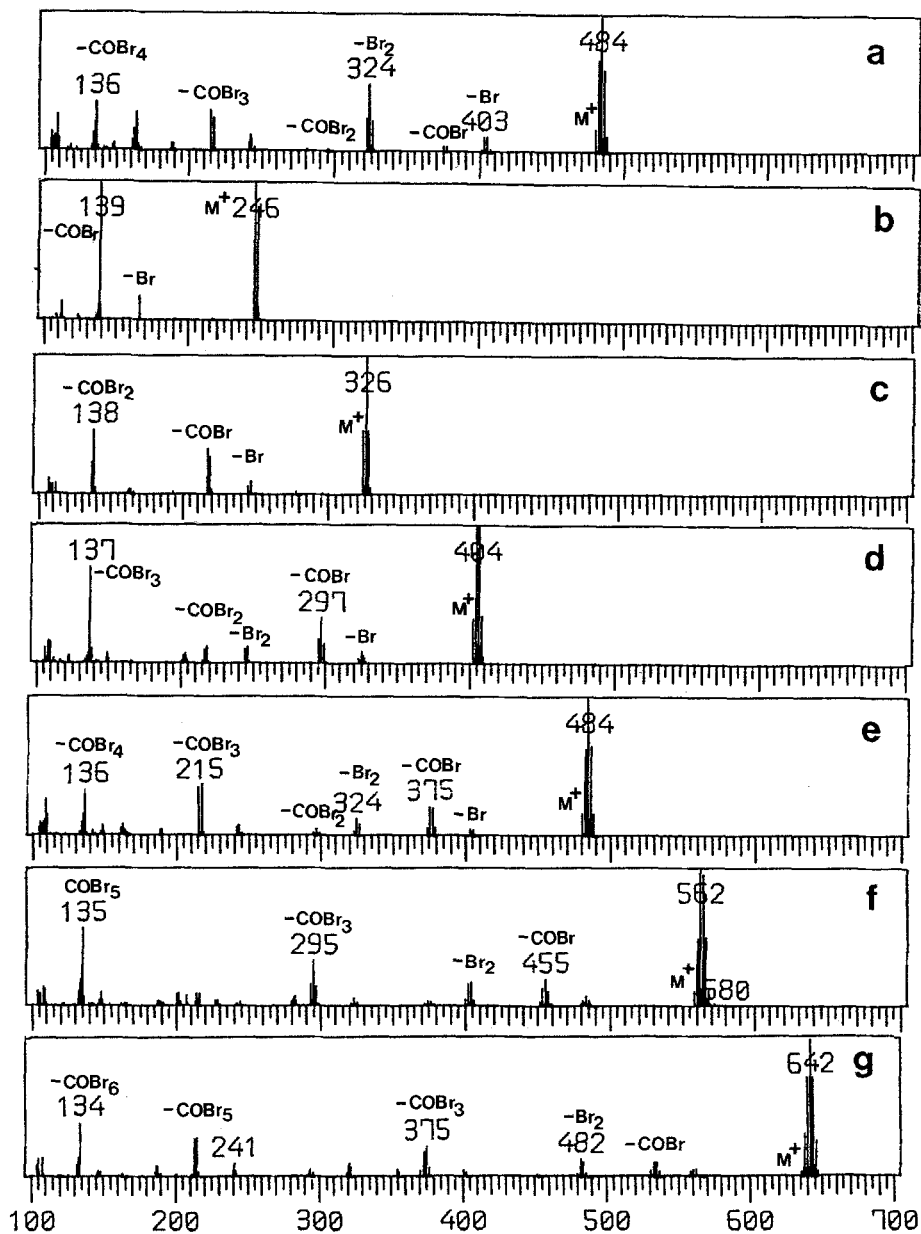


Figure 2. Mass spectra (EI, M/Z=100-700) of PBDFs: (a), 2,3,7,8-tetra-BDF standard; (b,c,d,e,f and g), main component peaks of 1F, 2F, 3F, 4F, 5F and 6F in Figure 1.

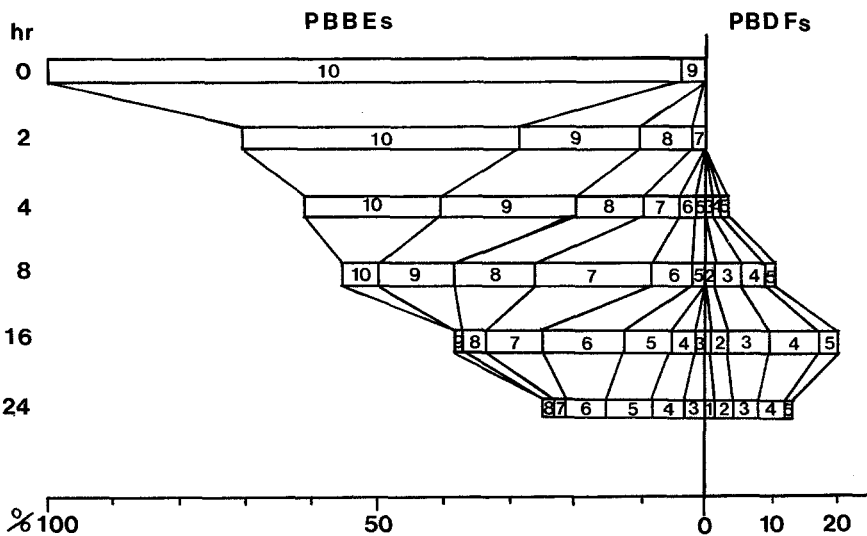


Figure 3. Schematic representation of the formation and disappearance of PBBEs and PBDFs in the UV photolysis of DBBE. The numbers indicate the numbers of substituted bromine atoms of PBBEs or PBDFs.

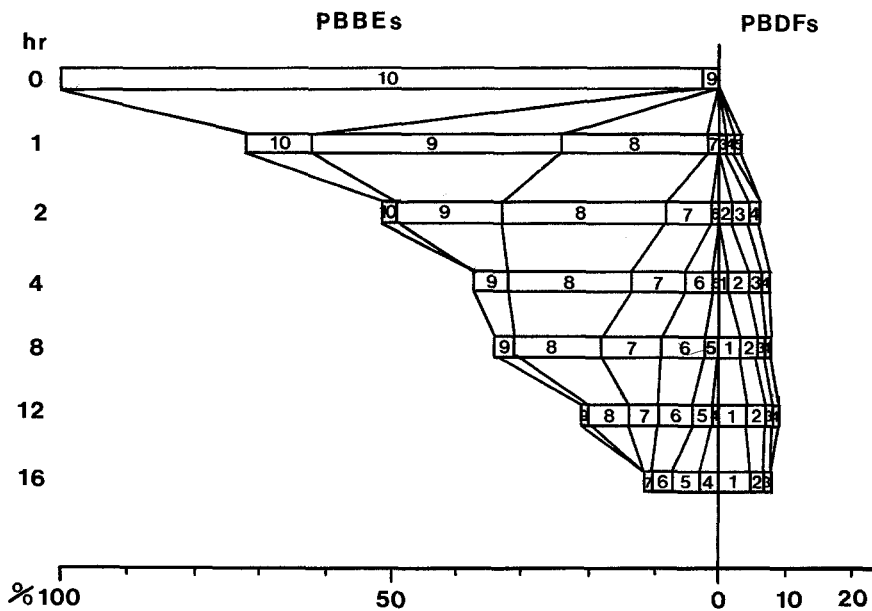


Figure 4. Schematic representation of the formation and disappearance of PBBEs and PBDFs in the sun light photolysis of DBBE. The numbers indicate the numbers of substituted bromine atoms of PBBEs or PBDFs.

the lack of agreement between the disappearance rate of DBBE and that of the formation of PBDFs. There was little or no accumulation of higher brominated dibenzofurans, especially hexa- to octabrominated species, in this system. Possibly debromination rather than cyclization occurred in DBBE and higher brominated biphenyl ethers by UV photolysis.

The total amount of PBDFs formed in this experiment was substantial, about a 20% yield for 16 hours UV irradiation, as shown in Figure 3. This yield was essentially the same as that by PCBEs photolysis, being a 10 - 20% yield, as reported by Choudhry et al.(1977). It is thus evident that halogenated dibenzofurans are the major products from halogenated biphenyl ether in UV photolysis.

Choudhry et al.(1977) reported the yields of dibenzofurans to increase in the presence of acetone on photolysis of PCBEs by UV (300nm dominant). However, this was not clearly detected in the present experiment.

Figure 4 shows schematically the results obtained from the sun light irradiation of DBBE. The formation and distribution of photoproducts by sun light were similar to those in UV irradiation, though a few differences could be recognized in both, i.e., the decomposition rate of DBBE, the total amount of and kinds of PBDFs formed, as shown in Figures 3 and 4. It is thus evident that the formation of PBDFs, in substantial yields, in the photolysis of DBBE by sun light is the same as that by UV photolysis.

Since the present experiment was carried out under laboratory conditions, it is premature to make definite conclusions regarding the formation of PBDFs from DBBE and debrominated compounds in the natural environment. However, DBBE and lower brominated biphenyl ethers have been confirmed as environmental pollutants both in Japan (Watanabe et al. 1986) and Sweden (Andersson and Blomkvist 1983). In addition, PBDFs have also been reported as the pyrolysis products of PBBEs by Buser (1986). Thus, the residue levels of both types of compounds in the environment should be investigated without delay.

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