

## The Photolysis of Halogenated Dibenzofurans in Hexane Solution and on Airborne Dust by Sunlight

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### 1. INTRODUCTION

The formation of polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) by heating or combustion of organobrominated flame retardants such as polybrominated biphenyl ethers (PBBEs)<sup>1,2)</sup> has become a matter of concern because of the new environmental problems arising out of these compounds in the world. Existing data suggested that toxicities of PBDDs/DFs are similar to those of their chlorinated analogues, i.e., polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)<sup>3)</sup>. These brominated products, predominantly PBDFs, are formed by the presence of PBBEs in workplace, during use, in building fire and municipal incinerators, although the production amounts depend largely on the combustion conditions.

Despite the existence of data on their formation, very few information is available on their occurrence, sources, distribution, dynamics and fate. A few earlier studies showed photolytic decomposition of some PBDDs/DFs standards dissolved in organic solvents<sup>4,5)</sup>, suggesting the possibility of photolysis in atmosphere as a major factor influencing the fate of PBDDs/DFs in the environment. Informations pertaining to dynamics and fate of PBDDs/DFs are necessary for environmental risk assessment and to estimate human exposure and toxicity evaluation.

In this study, in order to evaluate more clearly the atmospheric fate of compounds produced by combustion of PBBEs, the sunlight induced photolysis was conducted using standards dissolved in hexane and soil extract containing different kind of halogenated dibenzofurans such as PBDFs, PCDFs and bromo/chlorinated analogues (PXDFs). In addition, a preliminary study on photolysis of halogenated dibenzofurans in particulate phase by sunlight was made using airborne dust collected on a glass filter.

### 2. EXPERIMENT

#### (1) Samples and sunlight exposure

(A) Soil extract: Soil sample was collected from combustion site at metal reclamation factories located in Wan-Li, Southern Taiwan in 1991 (for samples details see reference 6). The final extract cleaned up for PCDDs/DFs analysis, in hexane solution, was used for

photolysis. Twenty ml of the soil extract in hexane was introduced into a quart tube (15 mm i.d. x 25 cm) and irradiated by sunlight. The approximate irradiation energy at 310 nm was about 400  $\mu\text{W}/\text{cm}^2$ . Two ml aliquots were removed from the solution at specified time intervals (0, 2, 4, 8, 16, 32, 64 min.) and then subjected for further determination.

(B) Standards: Standards in hexane were as follows; 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-tetra-CDF), 2-bromo-3,7,8-tri-CDF, 2,3,7,8-tetrabromodibenzofuran (2,3,7,8-tetra-BDF) 2,3,-dibromo-7,8-di-CDF and 1-bromo-2,3,7,8-tetra-CDF, 1,2,3,4,7,8,-hexa-BDF and 1,2,3,7,8,9-hexa-CDF.

(C) Air dust: Air dust was collected on a glass filter (200 mm x 250 mm) using a high volume air sampler at a flow rate of about 700 ml/min. for 24 hours in Osaka, Japan, in March 1994. Four glass filter samples were prepared and irradiated simultaneously. One fourth of each filter was cut off at 0 hr., 8 hrs. and 24 hrs. after irradiation. Filter samples cut off at each time were pooled together to one sample and subjected to extraction. Procedure for extraction and clean up of air dust was followed by the method described previously<sup>7)</sup>.

## (2) GC/MS analysis

A shimadzu 14 GC equipped with a DB-5 column (60 m x 0.25 mm i.d., 0.1 $\mu\text{m}$  film thickness. J&W) was employed for the analysis. The following conditions were used; injector temperature: 280  $^{\circ}\text{C}$ , Carrier gas: He at a head pressure of 1.75 kg/cm<sup>2</sup>, injection mode: splitless, oven temperature: 140  $^{\circ}\text{C}$ (2 min.) to 260  $^{\circ}\text{C}$  at a rate of 20  $^{\circ}\text{C}/\text{min}$ . and then to 310  $^{\circ}\text{C}$  at a rate of 3  $^{\circ}\text{C}/\text{min}$ .(15 min.). The HRMS used was Shimadzu-Kratos CONCEPT IS (Kyoto, Japan). The SIM conditions were as follows: ion source mode: EI, ion source temperature; 290  $^{\circ}\text{C}$ , electron energy; 44 eV, postacceleration detector: 8 kV, resolution: about 10000, the mass monitored for the analytes were chosen at two most intensive ions of molecular ion cluster.

## 3. RESULTS AND DISCUSSION

### (1)Photolysis of soil extract and standards in hexane solution

The results of photolysis of soil extract are shown in Table 1. Half-life of each compound was estimated by regression method of exponential equation. Tri- to hexa-CDF didn't reach their half-lives because of their stability or additional formation from higher halogenated congeners.

PBDFs in soil extract showed extremely rapid decomposition with half-lives in order of minutes, though PCDFs showed little degradation. It was recognized that their half-lives decreased with increasing number of bromine atoms. The major photochemical pathway was also confirmed to be reductive debromination by the photodegradation of hexa-BDF standard. These results agree well with those reported in previous studies<sup>4,5)</sup>.

Photolysis of polyhalogenated dibenzofurans substituted by the same number of halogens showed a decrease in their half-lives with increasing number of substituted bromine atoms (Table 1). On photolysis of monobrominated-PXDFs, decrease of their half-lives was recognized with increasing chlorine atoms, that is, increasing molecular weight (Table 1). In addition, it was confirmed that 1-bromo-2,3,7,8-tetra-CDF standard was debrominated leading to the formation of 2,3,7,8-tetra-CDF quantitatively. As shown in Table 1, tri-through penta-CDF showed an increase in their amounts with the irradiation time. It is therefore possible that most of the mono- and dibrominated PXDFs are debrominated and converted into additional PCDFs in the atmosphere.

Table 1. Sunlight induced photolysis of hexane extract of the soil collected from a combustion site in Taiwan.

Compounds	Relative amounts (% remaining)							Estimated Half-lives (min.)
	Control	Exposure time			( min.)			
		2	4	8	16	32	64	
Tri-CDF	100	99	109	111	125	140	151	NE
Bromo-di-CDF	100	108	116	111	117	85	59	46
Dibromo-mono-CDF	100	127	150	124	114	56	13	17
Tri-BDF	100	116	108	54	17	ND	ND	4.8
Tetra-CDF	100	95	98	94	104	117	126	NE
Bromo-tri-CDF	100	112	98	95	82	59	40	43
Dibromo-di-CDF	100	87	91	72	34	15	9	11
Tribromo-mono-CDF	100	94	75	43	20	ND	ND	6.5
Tetra-BDF	100	87	58	27	7	ND	ND	4.0
Penta-CDF	100	101	103	104	103	114	122	NE
Bromo-tetra-CDF	100	97	79	65	49	30	22	18
Dibromo-tri-CDF	100	75	65	32	22	14	6	4.9
Tribromo-di-CDF	100	79	62	33	13	7	ND	5.4
Tetrabromo-mono-CDF	100	71	45	17	ND	ND	ND	3.1
Penta-BDF	100	71	40	13	ND	ND	ND	2.7
Hexa-CDF	100	106	96	103	101	103	89	NE
Bromo-penta-CDF	100	92	80	51	34	29	18	9.8
Dibromo-tetra-CDF	100	90	69	39	26	15	10	5.7
Hepta-CDF	100	100	97	106	92	98	80	219
Bromo-hexa-CDF	100	79	73	53	38	26	19	12
Octa-CDF	100	90	90	86	94	78	63	98

NE: couldn't be estimated because of little change or additional formation.

ND: not detected.

## (2) Photolysis of halogenated dibenzofurans on airborne dust

Most of halogenated dibenzofurans in atmosphere is considered to be present as particles absorbed on airborne dust. Thus, it is worth to study the photodegradation of these compounds in particulate phase in the atmosphere. More than ten kind of PXDFs as well as PBDFs and PCDFs were found at the 0 hr. irradiated dust sample. Figure 1 shows the changes in these halogenated dibenzofuran components during the experiment period. The lower halogenated isomers of PXDFs, PBDFs and PCDFs decreased more largely (Figure 1). Most of the decrease in these components is seemed to be due to their evaporation because of larger disappearance of smaller molecular weight compounds with high vapor pressure. On the other hand, hepta-CDF and octa-CDF showed little disappearance during the experiment period. Monobromo-hepta-CDF and penta-BDF, which were expected to have behaved almost like hepta-CDF or they have lower vapor pressures than hepta-CDF, showed larger loss than the latter. Therefore, these two compounds might have been degraded by the photolysis. Half-lives of monobromo-hepta-CDF and penta-CDF on airborne dust were estimated to be scores of hours approximately. Lutas<sup>8)</sup> reported that PBDDs and PBDFs on actual soot particles were stable or degraded slowly over a period of hours. Therefore, it is concluded that halogenated dibenzofurans on real airborne dust should also have been degraded by sunlight though very slowly.

## 4. CONCLUSION

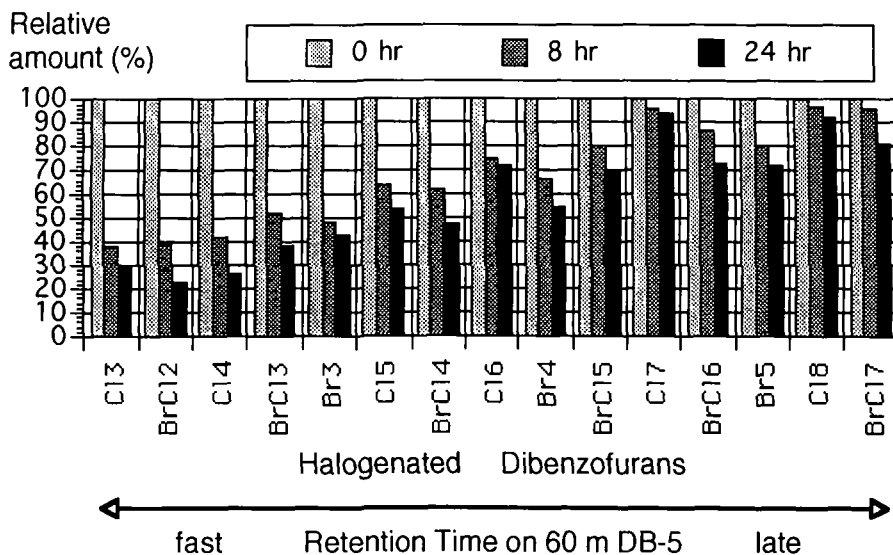


Figure 1. Photodegradation of halogenated dibenzofurans on airborne dust by sunlight. (Congeners are arranged in order of retention time 60m DB-5 column)

All of PBDFs and PXDFs in hexane solution were decomposed very rapidly by sunlight with half-lives in the order of minutes, though PCDFs showed little degradation. In addition, these brominated compounds absorbed on airborne dust were also estimated to be degraded by sunlight though their half-lives were in the order of hours. Therefore, stabilities of PXDFs and PBDFs in the atmospheric environment are considered to be lower than those of PCDFs, because of their rapid photodegradation. Although some of PXDFs convert into more stable PCDFs in atmosphere, few other PXDFs and PBDFs may be considered to be less transportable and more confined pollutants than PCDFs

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