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The Liquid-Phase Photolyses of Tetra- and Octa-CDDs and Their CDFs in Hexane Solution

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The liquid phase photolyses were conducted with a hexane solution of tetra- and octa-CDD and their CDFs at 254 nm. Their first-order rate constants obtained were as follows (x 10^{-5} s^{-1}): 2,3,7,8-TCDD, 29.2; 1,2,3,4-TCDD, 13.1; 2,3,7,8-TCDF, 46.0; octa-CDD, 17.7. The PCDF photolyses of 2,3,7,8-tetra- and octa-congeners compared to their CDDs were more rapidly, as well as the photodestructions of 2,3,7,8-chlorine substituted DD and DF which are more highly toxic substances.

Recently, the risk assessments for polychlorinated dibenzo-p-dioxins(P-CDDs) and dibenzofurans(PCDFs) are being conducted in various countries,1) because of their highly toxic effects,2) and because that their presences were confirmed in various combustion sources,3) airborn particles,4) indoor air,5) daily foods,6,7)mother's milk,8)and human body.9) Furthermore, there have been several reports on the PCDD/F destruction and their control technics.10) In addition to the development of an advanced technique for PCDD/F reduction,the photokinetics are necessary to study their behaviors and fate in the source and environment. We report here the liquid-phase photolyses of PCDDs/PCDFs in n-hexane solution at 254 nm, using the gas chromatography/mass spectrometry/single ion monitor(GC/MS/SIM).

Hexane was of reagent grade quality and obtained from Wako Pure Chemical Industries. 2,3,7,8- and 1,2,3,4-tetra-CDDs, octa-CDD, and internal standards(ISs), 1,2,3,4-tetra-CDD($^{13}C_6$) and octa-CDD($^{13}C_{12}$), were supplied by Cambridge Isotope Laboratories (Woburn, MA, USA). The highly purified 2,3,7,8-tetra-CDF and octa-CDF were provided for the quantitative analysis by Dr. Masuda (Daiichi College of Pharmaceutical Sciences). Three photocells(quartz: pathlength,10 mm; thickness,1.0 mm) were arranged around a vertical lamp (low pressure mercury lamp; wavelength, λ =254 nm, 15 W;

Toshiba) at an angle of 90 and 10 cm exposure distance (average 1050 μW/cm^2), respectively. Two sets of these instruments were placed in a controlled chamber with a fan(15±2℃). Each standard sample of PCDDs and PCDFs was prepared with hexane in the photocell at the optional concentration (1-10 ppm). The photoexperiments for each sample were simultaneously performed by using both three photocells irradiated and three "dark" cells as blank. After irradiation, 10 ng of tetra- or octa-IS was added to hexane solution in six photocells for GC/MS determination. Then, tetra- and octa-IS were used for the measurements of tetra-CDDs and -CDF and/or of octa-CDD and -CDF. Five μl of solution from each cell was sampled for GC/MS analysis. These procedures were repeated by each data point. The analytical conditions of GC/MS/SIM used to determine PCDDs and PCDFs are described elsewhere.[11)] All 12 or 18 data for each sample tested were obtained from 4 or 6 data points, including 3 data before irradiation.

Table 1. Photolysis Rate Constants and Half-lives for PCDDs and PCDFs in Hexane Solution

Test PCDDs and PCDFs	Rate constants $K_{p,254\ nm}$ x $10^{-5}/s^{-1}$	Correlation factors r	Half-lives $t_{1/2}$ h	Rel$^{a)}$ $t_{1/2}$	Toxic factors$^{b)}$
2,3,7,8-TCDD(10 ppm)	29.2	0.995	0.660	1.0	1.0
2,3,7,8-TCDF(1 ppm)	46.0	0.999	0.418	0.63	0.1
1,2,3,4-TCDD(1 ppm)	13.1	0.996	1.47	2.23	0
OCDD(10 ppm)	17.7	0.976	1.09	1.65	0.001
OCDF(5 ppm)	502.	0.972	0.038	0.06	0.001

a) Normalized with respect to 2,3,7,8-TCDD half-life. b) I-TEFs, 1989.

The first-order rate constants of PCDD and PCDF standards in hexane solution and their half-lives are shown in Table 1. The photolysis of 2,3,7,8-tetra-CDF(1 ppm)($46.0\mathrm{x}10^{-5}$ s^{-1}, r=0.999) occurred more rapidly, as compared to the PCDD photolyses, although the concentration of each sample was different. The photodestruction of 2,3,7,8-tetra-CDD was faster than that of 1,2,3,4-tetra-CDD, and its half-life (approximately 40 min) was rather shorter, as compared to octa-CDD. For octa-CDF (5 ppm) the significantly rapid photolysis($502.\mathrm{x}10^{-5}$ s^{-1}, r=0.975) was exhibited. The PCDF photolyses of 2,3,7,8-tetra- and octa-congeners compared to their CDDs were more rapid. 2,3,7,8-TCDD toxic equivalent factors(I-TEFs)[12)] are noted in Table 1. It was suggested that 2,3,7,8-tetra-CDD and -CDF, which are more highly toxic substances than other PCDD and PCDF isomers, were rapidly photolyzed. For rapid OCDF photolysis data, it is now in our investigation.

Desideri et al.[13)] have reported that the photolysis of 2,3,7,8-tetra-CDD in isooctane, hexane and cyclohexane solutions at 254 nm, and its half-life in hexane was equal to 150±28 min. This half-life was different from our result(about 40 min for 2,3,7,8-tetra-CDD). However, this might be caused by the different exposure distance(ref.;25 cm) and radiant energy (ref.;600 μ W/cm^2) used. For the photolysis in water/acetonitrile(2:3v/v) at 313 nm,[14] the first-order rate constants(x10^{-6} s^{-1}) of 1,2,3,7- and 1,3,6,8-tetra-CDDs and octa-CDD (molar extinction coefficient, $\varepsilon_{\lambda=313\ \mathrm{nm}}$ = 4,182 l mol^{-1} cm^{-1} in neat acetonitrile) were 18.13 ± 1.40, 59.57 ± 2.81 and 1.06 ± 0.14. From similar photolysis conducted with a solution of 2,3,7,8-tetra-CDD ($\varepsilon_{\lambda\ (\mathrm{max.})=309\ \mathrm{nm}}$ = 7,020 l mol^{-1} cm^{-1} in acetonitrile and $\varepsilon_{\lambda\ (\mathrm{max.})=304\ \mathrm{nm}}$ = 5,640 l mol^{-1} cm^{-1} in hexane) in water/acetonitrile(90:10) at 313 nm,[15] it has been shown that its rate constant, quantum yield and conversion rate at 24 h were (14.6 ± 0.9)x10 $^{-6}$s $^{-1}$, 0.002 and 62%, respectively. Although there is different by one to two orders of magnitude between these values and our results for tetra- and octa-CDD photolysis rates, it cannot be directly compared without considering the solvent and light source used. For the sunlight photolysis conducted with a solution of octa-CDD in hexane(approximately 1 μ l/ml),[16] its half-life was found to be 7.0 h in the beginning of August and 9.0 h in mid September. Furthermore, half-lives of 2,3,7,8-, 1,3,6,8-, and 1,2,3,4-tetra-CDDs and octa-CDD were 0.95, 8.45, 21.6, and 24.3 h, respectively, in n-hexadecane at 1.0 m exposure distance from sunlamp(wavelengths= 280-380 nm).[17] For our photolyses in hexane at 254 nm, tetra- and octa-CDDs and their CDFs were more rapidly photolyzed, as compared to above reference data.

Mass fragmentograms of photoproducts produced by the photolysis of octa-CDD are shown in Fig. 1. The concentration changes of 2,3,7,8-tetra-CDD and -CDF and photoproducts are shown in Fig. 2. According to the photo-

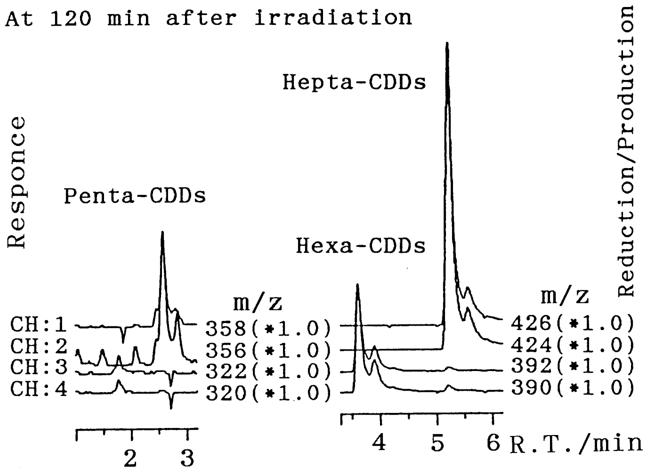

Fig. 1. Mass fragmentograms of products formed by the photolysis of octa-CDD.

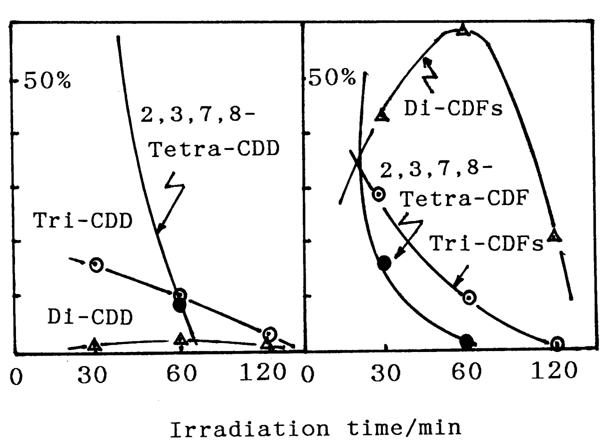

Fig. 2. Concentration changes of products by the 2,3,7,8-tetra-CDD and -CDF photolyses.

decompositions of the samples tested, it was observed that highly chlorinated DDs/Fs were successively changed to more lowly chlorinated ones, showing the differences in the production rates and induction periods of products and in the numbers of isomers produced. For the photolysis in acetonitrile and hexane,$^{18)}$ it has been also suggested that DD was rapidly transformed through a cascade of hydroxylated compounds to yield 2-hydroxybenzoic acid. This study(chief:Prof.,Dr.,Y. Takizawa) has been performed in 1987-1989 by the consignment of the Ministry of Health and Welfare, Japan.

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