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THE STUDY ON UV-DEGRADATION DYNAMICS OF 2,3,7,8-TETRACHLORODIBENZO-*p*-DIOXIN AND ITS ANALOGUES

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ABSTRACT

A study on UV-degradation dynamics of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8 - TCDD) and its analogues 2,3,7,8 - tetrachlorophenoxthin (2,3,7,8 - TCPT) and 2,3,7,8-tetrachlorothianthrene(2,3,7,8-TCTR) in solvents $CHCl_3$ and CCl_4 was completed. The results indicated that they were degradated by UV in different way in different solvent. The degradation of 2,3,7,8-TCDD and 2,3,7,8-TCPT are pseudo-first-order reactions in $CHCl_3$, but complex reactions in CCl_4; the degradation of 2,3,7,8-TCTR is a zero-order reaction in $CHCl_3$, but a pseudo-first-order reaction in CCl_4. All of the three compounds disappeared in CCl_4 much faster than in $CHCl_3$ under 254nm UV-irradiation. Copyright © 1996 Elsevier Science Ltd

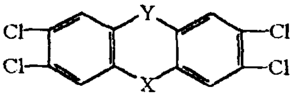
Key words: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; 2,3,7,8-tetrachlorophenoxthin; 2,3,7,8-tetrachlorothianthrene; UV-degradation

INTRODUCTION

The contamination of our environment by polychlorinated dibenzo-*p*-dioxins(PCDDs) is well known[1]. As the most toxic member of PCDD's family, the photodegradation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin(2,3,7,8 -TCDD) to a less toxic form is an important way in the determination of its environmental fate, as well as for remediation purposes.. Although several methods, such as oxidation[2], electrochemical decomposition[3], and microbial degradation[4], etc. had been investigated, TCDD was generally not satisfactory degraded because of its high stability and limitations on practical use of these techniques.

However, when Crosby *et al.*[5] irradiated TCDD in methanol or ethanol solution, substantial decomposition was observed. Similar results were also obtained by several other authors[6]-[9]. This exciting method was concluded that the minimum conditions necessary for TCDD photolysis were ultraviolet light and the presence of an organic hydrogen donor.

In the present studies the photodegradability of 2,3,7,8-TCDD in a non-hydrogen donating and a hydrogen donating solvent, CCl_4 and $CHCl_3$, respectively, was compared. Two analogues 2,3,7,8-TCPT and 2,3,7,8-TCTR were also studied for researching the influence of the parent heterocycle on photolysis. Their dynamic equations and the photolysis mechanisms were deduced.



(1) X=Y=O 2,3,7,8-tetrachlorodibenzo-*p*-dioxin
(2) X=O, Y=S 2,3,7,8-tetrachlorophenoxthin
(3) X=Y=S 2,3,7,8-tetrachlorothianthrene

EXPERIMENTAL SECTION

Materials

All compounds were synthesized and the melting points were uncorrected. MS was determinated on JMS-D300 and ^{1}H-NMR on JNM-GX400.

1.The synthesis of 2,3,7,8-tetrachlorodibenzo-p-dioxin

2,3,7,8-TCDD was synthesized as described by Andrew S. Kende[10]. Recrystalized three times with methyl phenyl ether. M.p. 303.5-5℃, yield 65.4%(Lit. M.p. 305-7℃, yield 41%), M/z 320(75), 322(100), 324(50). ^{1}H NMR(C_6D_6) δ_{ppm} 6.40(s, 4H). $C_{12}H_4Cl_4O_2$ requires: C 44.77%, H 1.24%, Cl 43.09%; Found: C 45.71%, H 1.21%, Cl 44.05%.

2. The synthesis of 2,3,7,8-tetrachlorophenoxthin

In a 100mL three-necked flask were placed 2.0g phenoxthin (synthesized as lit. described[11], M.p. 54.0-55.5℃, yield 35.4%; Lit. M.p. 57.5-58.0℃, yield 31%), 0.5g anhydrous $FeCl_3$ and 44.4g monochlorotoluene (ortho:para=1:1). A little excess of chlorine was introduced during three hours at 35℃ under stirring. After cooling to room temperature, the solid precipitated was collected, recrystalized three times with THF. 1.8g colourless needles was obtained. M.p. 224.6-5.7℃, yield 53.3%. M/z 336(75), 338(100), 340(5)). ^{1}H NMR(C_6D_6) δ_{ppm} 6.44(s, 2H), 6.55(s, 2H). $C_{12}H_4Cl_4OS$ requires: C 42.64%, H 1.19%, Cl 41.95%, S 9.48%; Found: C 42.40%, H 1.14%, Cl 41.25%, S 9.37%.

3. The synthesis of 2,3,7,8-tetrachlorothianthrene

In a 250mL three-necked flask were placed 4.0g thianthrene (synthesized as lit. described[12]. M.p. 156.7-8.1℃, yield 66.1%; Lit. M.p. 158-9℃, yield 65%), 0.1g anhydrous $FeCl_3$ and 88.8g *p*-chlorotoluene. A little excess of chlorine was introduced during 4.5 hours at 70℃ under stirring. After cooling, the solid precipitated was collected, recrystalized three times with THF. 3.1g product was obtained as white cotton crystals. M.p. 278.5-80.1℃, yield 47.0%. M/z 352(75), 354(100), 356(50). ^{1}H NMR (C_6D_6) δ_{ppm} 7.00(s, 4H). $C_{12}H_4Cl_4S_2$ requires: C 40.70%, H 1.14%, Cl 40.05%, S 18.11%; Found: C 40.23%, H 0.96%, Cl 40.98%, S 17.18%.

UV-degradation

1. Irradiation and detection

The light source selected for these studies was a 550 watt high pressure mercury lamp (Model BIZ-U). The light beam with a 254 nm wave length (λ) passes through water and reaches to the samples (the distance between sample and light source is 6cm). The procedure was completed in a constant temperature 25℃.

High performance capillary gas chromotography(HPCGC) and FID were used to determine the concentrations of the analytes during the course of UV-irradiation. *n*-Eicosane was used as an internal standard for 2,3,7,8-TCDD and 2,3,7,8-TCPT and triphenyl phosphate for 2,3,7,8-TCTR analysis.

2. determination of accuracy and precision of the method

Table 1. Determination of precision of the method (in CCl_3)

compound	2,3,7,8-TCDD(n=10)	2,3,7,8-TCPT(n=10)	2,3,7,8-TCTR(n=10)
mean area of peaks $\bar{X}$	1.7262	0.7351	1.6593
standard error σ	0.0960	0.0174	0.0220
relative standard error c.v.	4.00%	2.36%	1.33%

Table 2. Determination of accuracy of the method (in $CHCl_3$)

compound	No.	concn. compounded (mg/mL)	concn. detected $(mg/mL)_{n=5}$	percentage received (%)
2,3,7,8-TCDD	1	0.30	0.29	96.67
	2	0.09	0.09	100.00
	3	0.06	0.06	100.00
2,3,7,8-TCPT	1	0.70	0.70	100.00
	2	0.42	0.42	100.00
	3	0.28	0.27	96.43
2,3,7,8-TCTR	1	1.05	1.08	102.86
	2	0.63	0.64	101.59
	3	0.42	0.41	97.62

RESULTS AND DISCUSSION

Results

The results of UV-degradations of 2,3,7,8-TCDD and its analogues are listed in Table 3. and Table 4.

Table 3. UV-degradation of 2,3,7,8-TCDD and its analogues in $CHCl_3$ (25℃)

compound											
2,3,7,8-TCDD	irradn. time t(hrs)	0	10	16	22	28	34	40			
	concn. left C(mg/mL)	0.2485	0.1950	0.1732	0.1643	0.1301	0.1131	0.1059			
	% compound left	100.00	78.47	69.70	66.12	52.35	45.51	42.62			
	regrn. equation	$\ln C = -1.3953 - 0.02187t$								(1)	
	related coefficient γ	-0.9923									
2,3,7,8-TCPT	irradn. time t(hrs)	0	1	2	3	4	5	6	12	24	30
	concn. left C(mg/mL)	0.4800	0.3678	0.2634	0.2373	0.1868	0.1782	0.1637	0.0714	0.0182	0.0081
	% compound left	100.00	76.63	54.88	49.44	38.92	37.13	34.10	14.88	3.79	1.69
	regrn. equation	$\ln C = -1.0053 - 0.1281t$								(2)	
	related coefficient γ	-0.9953									
2,3,7,8-TCTR	irradn. time t(hrs)	0	1	2	3	4	5	6	7	19	25
	concn. left C(mg/mL)	0.6220	0.6050	0.6028	0.5750	0.5680	0.5552	0.5548	0.5480	0.4007	0.3176
	% compound left	100.00	97.27	96.91	92.44	91.32	89.26	89.20	88.10	64.42	51.06
	regrn. equation	$C = 0.6204 - 0.0119t$								(3)	
	related coefficient γ	-0.9976									

Discussion

1. Apparent dynamic equations, $t_{1/2}$, $t_{90\%}$, $t_{99\%}$

Differential and alternate equations (1) to (6), apparent dynamic equations of degradation reactions of compound (1), (2) and (3) in $CHCl_3$ and CCl_4 respectively can be obtained. $t_{1/2}$(half life), $t_{90\%}$ and $t_{99\%}$(the time degradating the material 90% and 99% respectively) are also obtained from equations (1) to (6). Results calculated are listed in Table 5.

Table 4. UV-degradation of 2,3,7,8-TCDD and its analogues in CCl_4 (25℃)

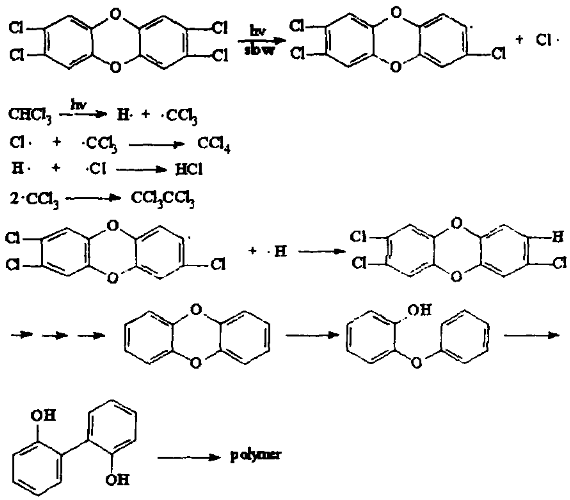
compound									
2,3,7,8-TCDD	irradn. time t(hrs)	0	1	2	3	4	5	6	7
	concn. left C(mg/mL)	0.2400	0.2231	0.2147	0.2007	0.1647	0.0802	0.0587	0.0213
	% compound left	100.00	92.96	89.46	83.63	68.63	33.42	24.46	8.88
	regrn. equation	$\ln C = -1.4580 - 0.0069t^3$						(4)	
	related coefficient γ	-0.9935							
2,3,7,8-TCPT	irradn. time t(hrs)	0	1	2	3	4	5		
	concn. left C(mg/mL)	0.3968	0.3514	0.3096	0.2128	0.0859	0.0559		
	% compound left	100.00	88.56	78.02	53.63	21.65	14.09		
	regrn. equation	$\ln C = -0.9164 - 0.0824t^2$						(5)	
	related coefficient γ	-0.9883							
2,3,7,8-TCTR	irradn. time t(hrs)	0	1	2	3	4	5	6	
	concn. left C(mg/mL)	0.4228	0.3213	0.2383	0.1880	0.1520	0.1308	0.0994	
	% compound left	100.00	75.99	56.36	44.47	35.95	30.94	23.51	
	regrn. equation	$\ln C = -0.9123 - 0.2354t$						(6)	
	related coefficient γ	-0.9960							

Table 5. Apparent dynamic equations of the UV-degradation reactions

compd.		2,3,7,8-TCDD	2,3,7,8-TCPT	2,3,7,8-TCTR
apparent dynamic equation	$CHCl_3$	$\frac{dC}{dt} = -0.02187C$	$\frac{dC}{dt} = -0.1280C$	$\frac{dC}{dt} = -0.0119$
	CCl_4	$\frac{dC}{dt} = -0.38C(\ln C+1.458)^{2/3}$	$\frac{dC}{dt} = -0.574(-\ln C - 0.9164)^{1/2}$	$\frac{dC}{dt} = -0.2354C$
$t_{1/2}$ (hrs)	$CHCl_3$	31.6	3.3	26.0
	CCl_4	4.6	2.9	2.7
$t_{90\%}$ (hrs)	$CHCl_3$	105.1	15.9	46.9
	CCl_4	6.9	5.3	9.6
$t_{99\%}$ (hrs)	$CHCl_3$	210.4	33.9	51.6
	CCl_4	8.7	7.5	20.0

2. Mechanism of the decomposition reaction

The decomposition rates of the three compounds in CCl_4 were considerably faster than in $CHCl_3$. It was obviously that they might be degradated in different way within different solvents. The photolysis might be involved in the cleavage of C-Cl bond and C-X or C-Y bond in both media. Most probably, as Mamantov[13] and Masakazu Makino *et al.*[14][15] proposed, the cleavage of C-Cl bond to yield an aryl radical and the substitution of Cl by H step-by-step was the major pathway for TCDD in $CHCl_3$. The solvent acted as a hydrogen donor in the reaction. Our studies show that the 2,3,7,8-TCDD photolysis data in $CHCl_3$ was best fit by a pseudo-first-order reaction. This was of the same view with the other authours' conclusions undergone in the other hydrogen-contaning solvents.



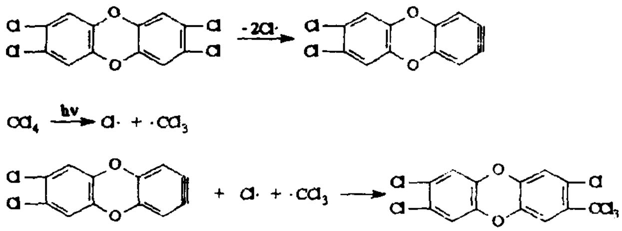
$CHCl_3 \xrightarrow{hv} H\cdot + \cdot CCl_3$

$Cl\cdot + \cdot CCl_3 \longrightarrow CCl_4$

$H\cdot + \cdot Cl \longrightarrow HCl$

$2\cdot CCl_3 \longrightarrow CCl_3CCl_3$

What happened for TCDD in CCl_4 may be more complex. A reasonable mechanism may be involved the formation of a benzyne intermediate.



$CCl_4 \xrightarrow{hv} Cl\cdot + \cdot CCl_3$

Unfortunately, only 2,3,7-trichlorodibenzo-*p*-dioxin , HCl and CCl_3CCl_3 had been seen by GC/MS in the course of TCDD degradation in $CHCl_3$ because of low sensitivity of the mass spectrometer. The mechanisms were still conjectural because lack of some neccessary information.

According to the apparent dynamic equations, it is found that the parent heterocycles affects the photolysis not only in the reaction rate but also the mechanism. The cleavage of C-S bond also may be important for TCPT and TCTR both in $CHCl_3$ and CCl_4.

CONCLUSIONS

According to the research, several important conclusions can be drawn although the disappearance of parent compound is the only criterion. First, these compounds can be photodegraded in a non-hydrogen solvent (CCl_4) much faster than in a hydrogen one ($CHCl_3$). The presence of a hydrogen donor is not a necessary condition for photodegradation. The photochemical reaction is influenced by both medium and parent heterocycle. The cleavage of C-Cl bond may be the major pathway for TCDD. But the cleavage of C-S bond also may be important for TCPT and TCTR. A 254nm UV light, not a simulating sunlight, was used because a constant wavelength was better than a complex one in dynamic study, and on the other hand we wonder this facile equipment could be used conventionally to remove the polluents in laboratory. Although modification will be needed on practical use to clean up natural contaminated sites, these findings are usefull to environmental chemists for further evaluation about UV-degradation technique.

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