Mechanism Study on Oxidative Degradation of Typically PCDD/Fs in Atmosphere

大气中典型二噁英类物质的氧化降解机理研究

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Chenxi Zhang Xiaomin Sun
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Preface

Dioxins are the general term for polychlorodibenzo－*p*－dioxins (PCDDs) and polychlorodibenzofurans (PCDFs). Due to their properties of carcinogenesis, tetratogenesis and mutagenesis, and may enter human body through food chain and endanger the human health, PCDD/Fs have been enlisted in Stockholm Convention. The major sources of PCDD/Fs are waste incineration, chemical industry production, metal smelting and refining process, and paper manufacturing industry. The PCDD/Fs in the atmosphere are in the form of gas phase or particles, which are mainly influenced by saturated vapor pressure and temperature. At the ambient temperature, low chlorinated PCDD/Fs (mainly with six or less chlorine atoms) have high concentration in the gas phase, while high chlorinated PCDD/Fs (primarily hepta－ and octa－chlorinated homologues) mainly distributed in the particle phase. In the flue gas, 82%～93% of PCDD/Fs are distributed in the gas phase due to high temperature. The atmospheric fate for PCDD/Fs is removed from the atmosphere via the dry or wet deposition, photolysis and the reactions with the atmospheric oxidants (including OH radical, HO_2 radical, O_3, NO_3 radical, and Cl atom). Particle-phase

PCDD/Fs are removed from the atmosphere via the dry or wet deposition, while gas-phase PCDD/Fs are depleted via photolysis and degradation reactions. It is critical to know the reaction mechanism and accurate rate coefficients of PCDD/Fs with various oxidants in order to assess their dominant atmospheric fate.

Due to their toxicities and the rather low vapor pressure, the reaction mechanism and direct kinetic measurements of the reactions are difficult to obtain by experimental study. This book apply the method of theoretical study, which can provide accurate predictions for the reaction mechanism by calculating the energies and can generate kinetic data of key elementary reaction steps.

The first chapter introduces the properties, toxic effects, sources, concentrations and transformation of PCDD/Fs present in the environment.

The second chapter introduces the initiation reactions of 2,3,7,8-TCDD/F with OH radical, HO_2 radical, O_3, NO_3 radical, and Cl atom. The atmospheric lifetime τ of the 2,3,7,8-TCDD/F with respect to OH radicals, O_3, NO_3 radicals, and Cl atoms are also estimated, and the study show that 2,3,7,8-TCDD/F will be mainly scavenged by OH radical, while NO_3 radical is the primary oxidant at night and Cl atom dominates after sunrise in coastal and marine areas.

The third chapter introduces the OH-initiated atmospheric deg-

radation reaction of 2,3,7,8-TCDD in the presence of O_2 and NO/H_2O. The results show that more than 93% of the OH radical addition reaction for 2,3,7,8-TCDD occurs on C_γ. In the ensuing reactions of TCDD-OH, the bond cleavage of dioxin ring and O_2 addition are both important. The reaction with NO in atmosphere is the main removal way of the peroxy radical isomers TCDD-OH-O_2. The carbonyl free radicals can abstract H atom from H_2O to reach a stable state and the OH radical will be regenerated simultaneously, which can interprete the significantly increasing destruction efficiency of PCDD/Fs in the presence of water vapor.

The fourth chapter introduces the OH-initiated atmospheric chemical reaction mechanism and kinetics of 2,3,7,8-TCDF in the presence of O_2 and NO/H_2O. The reaction mechanism of 2,3,7,8-TCDF with OH radical and ensuing reactions including bond cleavage of furan ring, O_2 addition or abstraction, dechlorination process, bimolecular reaction of TCDF-OH-O_2 peroxy radical with NO and reaction of carbonyl free radicals TCDF-OH-O with H_2O are researched.

The fifth chapter introduces the quantitative structure-activity relationships study on the rate constants of polychlorinated dibenzo-p-dioxins with OH Rradical.

This book can serve as a template for atmospheric degradation of the gaseous PCDF congeners, which is helpful in assessing

their atmospheric behaviors.

The book was written by Doctor Zhang Chenxi from Binzhou University and Professor Sun Xiaomin from Shandong University. Professor Li Jialiang made a comprehensive and detailed review of the book. Doctor Zhang Jiqiang participated in compiling, entering, proofreading the book and etc.

Due to the limitation of time and academic level, there will be unavoidable shortcoming. Readers are welcome to criticize and suggest. The author is sincerely grateful to all of the authors of the references.

Chenxi Zhang

March 23. 2018

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1 Introduction

Polychlorinated dibenzo - p - dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively called dioxins, are two groups of tricyclic, planar, aromatic substances. In the case of PCDDs, the benzene rings are joined by two oxygen bridges, and in the case of PCDFs, the benzene rings are connected by a carbon bond and an oxygen bridge. Based on the number and positions of the chlorine atoms as shown in Figure 1.1, PCDDs and PCDFs consist of 75 and 135 congeners, respectively. The objectives of this work were as follows: (1) summarize the sources of PCDD/Fs; (2) briefly discuss the concentrations distributions in various compartments; and (3) identify the transformation pathways affecting the behavior of PCDD/Fs. This integrative review tries to give a synopsis of PCDD/Fs science, which is help for decision making for environmental managers.

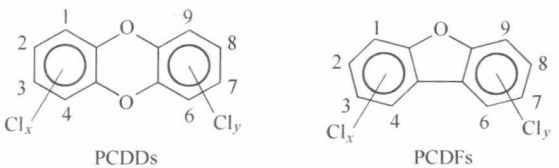


Figure 1.1 Chemical structure of PCDDs and PCDFs

1.1 Physical and chemical properties

PCDD/Fs show low water - solubility ($7.4 \times 10^{-8} \sim 4.3 \times 10^{-4}$ mg/L at 298K) and high values for the organic carbon/water partition coeffcient ($K_{oc} = 0.41$) and the octanol/water partition coeffcient ($\lg K_{ow} > 5.0$)[1]. Hence, they accumulate in media rich in organic carbon, such as soils and sediments.

The vapor pressure of PCDD/Fs decreases with an increasing degree of chlorination, as presented in Table 1. 1.

Table 1. 1 Typical physical and chemical properties of PCDD/Fs[2]

Homologue group	Water solubility (mg/L at 298K)	$\lg K_{ow}$	Vapour pressure (mmHg at 298K)
TCDD	3.5×10^{-4}	6.4	8.1×10^{-7}
PeCDD	1.2×10^{-4}	6.6	7.3×10^{-10}
HxCDD	4.4×10^{-6}	7.3	5.9×10^{-11}
HpCDD	2.4×10^{-6}	8.0	3.2×10^{-11}
OCDD	7.4×10^{-8}	8.2	8.3×10^{-13}
TCDF	4.2×10^{-4}	6.2	2.5×10^{-8}
PeCDF	2.4×10^{-4}	6.4	2.7×10^{-9}
HxCDF	1.3×10^{-5}	7.0	2.8×10^{-10}
HpCDF	1.4×10^{-6}	7.9	9.9×10^{-11}
OCDF	1.4×10^{-6}	8.8	3.8×10^{-12}

In the atmosphere, the PCDD/Fs partition between the gas and particle phases, with the major determining factor being the liquid-phase vapor pressure at ambient temperature. Based on theoretical considerations of gas-particle partitioning and the results of several ambient air studies, at 298K the PCDD/Fs with four or less chlorine atoms are expected to be present mainly in the gas phase, with DD and DF being 100% in the gas phase, the penta- and hexa-chloro-isomers being present between gas and particle phases and the hepta- and octachloro-isomers being predominantly in the particle phase[3,4].

1.2 Toxic effects

The toxicity of PCDD/Fs varies with the number of chlorine atoms and substituent positions. 2378-TCDD, as "the most toxic man-made chemical", was classified in 1997 by the International Agency for Research on Cancer (IARC) as a level 1 carcinogen for humans. In order to achieve a higher level of uniformity and comparability of results defining PCDD/Fs content

in samples of different materials of different origin, there was adopted the International Toxicity Equivalent Factor (I-TEF).

The first set of factors referred to as the I-TEF were established by a NATO/CCMS Working Group on Dioxins and Related Compounds to calculate Toxic Equivalent (TEQ). The resulting TEQs for all dioxin congeners measured in a sample are then added together to determine the total dioxin TEQ concentration for that sample. In 1997, TEQs were evaluated by the World Health Organization/Intergovernmental Programme on Chemical Safety and changes to TEFs were made for 1,2,3,7,8-PeDD, 1,2,3,7,8-PeDF, OCDD and OCDF. In addition, TEF values were established for birds and fish. These set of TEFs are referred to as WHO-TEF. In 2005, the TEFs were again evaluated by an expert group and based on new toxicity data, as shown in Table 1.2[5]. Of those 17 PCDD/F congeners, three congeners have the highest toxic equivalents contributing to 99% of the total toxic equivalent. These are 2,3,7,8-TCDD (TEF=1), 1,2,3,7,8-PeCDD (TEF=1), and 2,3,4,7,8-PeCDF (TEF=0.3). In comparison to white arsenic and cyanic potassium, 2,3,7,8-TCDD is 900~1000 and 100~1000 times more toxic, respectively[6].

Table 1.2 Toxic equivalency factors to express the toxicity of mixtures of PCDDs, PCDFs in toxin equivalents of 2,3,7,8-TCDD (WHO-TEF)[5]

Structure	WHO-TEF (1998)	WHO-TEF (2005)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.0003
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03

Continued 1.2

Structure	WHO-TEF (1998)	WHO-TEF (2005)
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	0.0003

PCDD/Fs produce a wide variety of species specific effects including immunotoxicity, hepatotoxicity, endocrine disruption, teratogenesis, and tumor promotion[7-9]. PCDD/Fs exert their effects via high-affinity binding to a specific cellular protein known as the aryl hydrocarbon receptor (AhR). The AhR is an intracellular ligand activated transcription factor involved in regulation of the expression of a large number of genes. The activated form of the AhR also interacts with other regulatory proteins such as specific cellular kinases, cell cycle control proteins, and other proteins involved in apoptosis[10,11].

1.3 Dioxins sources

The dioxins can be formed through natural sources. Biological formation of PCDD/Fs in sediments and soils has been confirmed. Svenson et al. found that Horse - redish peroxidase enzyme could convert chlorophenol into PCDD/Fs[12]. Oberg and Rappe, and Schramm et al. have also noted the potential for the natural formation of PCDD/Fs in sewage sludge and compost, which are synthesised by peroxidates from chlorinated organic precursors such as chlorophenols[13,14].

Forest fires and volcanoes are also come under this category. Gullett et al. conducted several burn tests on forest biomass, and found that PCDD/F

emission factors ranging from 0.3 to 26.3 ng TEQ/kg carbon burned, with a mean and median of 5.8 and 3.3 ng TEQ/kg carbon burned, respectively[15]. The majority of the PCDD/F partitions to the emissions rather than the ash.

In addition, a wide range of dioxin levels in clay was found, including many non-contaminated clay samples. Kaolinitic clay from the Westerwald area in Germany was found to contain several hundred ng I-TEQ/kg[16]. The dioxin pattern also found in different regions of the world: in the Mississippi basin (where the ball clay was mined), in the Westerwald area of Germany (where the kaolinitic clay was mined) and in sediments from the East coast of Australia. It is probable that the geothermal processes formed this unique pattern of PCDD/Fs over time from organic material and chlorine[17].

But above all, PCDD/Fs released to the environment are mainly from anthropogenic activities, including incineration precesses, pyrometallurgical processes, coal fired power generation, chemical manufacturing, open burning of electronic waste, biomass burning, vehicular emission and kiln-firing of ball clay.

1.3.1 Incineration processes

The major forms are municipal solid waste incinerators, hospital waste incinerators, hazardous waste incinerator and sewage sludge incinerator. It was observed that several past studies demonstrated the presence of PCDD/Fs and their precursors in municipal solid waste around 0.05 ng I-TEQ/g[18]. The average PCDD/Fs concentrations of stack gases from two large-scale municipal solid waste incinerators (MWIs) in Taiwan are 0.17 and 0.043 ng I-TEQ/Nm^3, respectively[19]. While the PCDD/Fs concentrations of the stack gas produced from one hospital waste incinerator (HWI) and one industrial hazardous waste incinerator (IHWI) were 17.7 and 0.7 ng I-TEQ/Nm^3, respectively[20]. Thus, the output from hospital waste incineration is much higher. The limitations facing land filling and recycling and

the planned ban on sea disposal has led to the use of incineration processes for the disposal of sewage sludge, which is the solid residue with high organic and toxic metal contents. A few studies were reported on the sewage sludge incineration[21].

1.3.2 Pyrometallurgical processes

The steel and nonferrous productions, including iron ore sintering process (Sinter), electric arc furnace (EAF), secondary copper production (SCu), secondary aluminum production (SAl) and secondary lead production (SPb) are found to be typical sources of dioxins.

Besides, stack gas samples at different smelting stages (feeding-fusion, oxidation and deoxidization) were collected from four plants[22]. The results indicated that the concentrations of PCDD/Fs in the stack gas were in the range of 0.009 ~ 1.29 ng TEQ/Nm^3. And PCDD/F emissions occur mainly at the feeding-fusion stage and these emissions contribute to 54% ~ 88% of the total emissions from the secondary copper smelting process.

1.3.3 Coal fired power generation

The dominant sources of PCDD/Fs in the KC area (Taiwan) are the coal-fired power plants, secondary aluminum smelting, electric arc furnaces, and open burning of rice straw, which contributed for 56%, 17%, 13%, and 3.3% to the total, respectively[23].

Paradiz et al. show that the coal combustion in domestic stove when combusting high chlorine coal (0.31%) can result in extreme concentrations of PCDD/F concentrations (over 100 ng TEQ/m^3), while the PCDD/F concentrations in the flue gases dropped below 0.5 ng TEQ/m^3 when low chlorine coal (0.07%) was used[24].

1.3.4 Chlorinated-chemical industrial processes

The release of PCDD/Fs as by-products from the manufacture of chlorinated compounds such as chlorinated pesticides and herbicide, chlo-

rinated benzenes, chlorinated phenols, PCBs, chlorine bleached wood pulp and chlorinated aliphatic compounds has been identified as a major source of environmental contamination[25-28].

The total concentrations of 2,3,7,8-PCDD/Fs in the 2,4-D samples ranged from 0.355 to 35.080 ng/g and the corresponding TEQ values were in the range of 0.013 and 0.69 ng TEQ/g[29]. In addition, the TEQ levels of PCDD/Fs in Chinese Pentachloronitrobenzene (PCNB) products were 0.26~0.93 ng TEQ/g[30].

1.3.5 Open burning of electronic waste

The electronic waste may significantly contribute to emissions of PCDD/Fs to air because much of the e-waste contains PVC. It was estimated that the largest type of plastics used by volume (26%) in electronics manufacturing was PVC and was used in computer cable and computer housing. Studies have also shown that the combustion of plastics, particularly PVC, in the presence of a copper catalyst generate PCDD/Fs[6].

1.3.6 Biomass burning

Biomass burning has been identified as an important emission source of PCDD/Fs to the environment[31]. Gullett and Touati tested the rice-straw smoke of the rice straw grown in California, and estimated that the PCDD/Fs emission factor of rice straw burning was approximately 0.5 ng-TEQ/kg of the burned[32]. Further, Shih et al. reported that the TEQs of the PCDD/Fs present in the ambient air during the rice straw burning season were 4-17 times those in other seasons in southern Taiwan[33].

1.3.7 Vehicular emission

Vehicular exhausts may also contribute to increases in overall PCDD/Fs concentrations in ambient air. In a previous study made from Valerenga tunnel, Oslo, the dioxin emission factor of a heavy duty vehicle was found to be much higher than that of a light duty vehicle[34]. According to some la-