

## Formations of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans during Thermo-Chemical Reactions of Polychlorinated Alkylphenoxyalkylphenols

Sukeo Onodera, Manami Fukazawa, Mari Tatsuno, Hiroaki Nakano, Takuya Kitao, and Kazumi Fujimori. Faculty of Pharmaceutical Sciences, Tokyo University of Science, Shinjuku-ku, Tokyo 162 JAPAN

### Abstract

Pyrolysis products of polychlorinated alkylphenoxyalkylphenols (alkyl PCPPs), which have been shown to be present in the aqueous chlorination products of alkylphenols, in a quartz reaction tube at 300~700°C for 3 min under an air stream were analyzed by GC/MS for PCDDs, PCDFs and related compounds. These alkyl PCPPs were found to be converted into three types of compounds, including PCDDs and PCDFs upon heating over 400°C for 3 min. The compositions and amounts of PCDDs and PCDFs formed from alkyl PCPPs were strongly dependent upon the pyrolysis conditions such as heating temperatures.

### Introduction

PCDDs and PCDFs are groups of hazardous compounds, among of which are some extremely toxic isomers. During recent years, PCDDs and PCDFs have received scientific and public attention. PCDDs and PCDFs are trace contaminants of certain industrial chemicals such as chlorophenols, polychlorinated biphenyls (PCBs) and other chlorinated aromatics. In addition, PCDDs and PCDFs can be formed from these industrial chemicals in substantial yields in the thermal reactions. This conversion into PCDDs and PCDFs has been shown for the chlorophenols, PCBs, polychlorinated diphenyl ether's (PCDPEs). However, contribution of these chemicals to the formation and presence of PCDDs and PCDFs in the MSW combustion processes are not yet clear in the literature.

Irgasan DP300 (triclosan: 5-chloro-2-(2,4-dichlorophenoxy)phenols) is widely used for the preservation of cosmetic products and as antimicrobial agent for textile products. This compound is also known as the predioxin in the thermal (1) and photochemical reactions (2). In our recent findings (3, 4) have demonstrated that phenolic compounds react with chlorine in water to form polychlorinated phenoxyphenols (PCPPs) and alkyl PCPPs including predioxins and isopredioxins. The data present here show the formation of PCDDs and PCDFs and related compounds during thermo-chemical reactions of these chemicals.

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## Experimental Methods

Irgasan DP300 was commercially available (purity, over 99%) and employed as a standard predioxin. Several PCPPs and alkylated PCPPs were prepared according to the method described in the previous papers (3, 4) and summarized in Table I. Each material dissolved in diethyl ether (5 mg/ml) were placed on a quartz sample boat and dried under nitrogen gas stream. The boat was introduced in a quartz reaction tube (20 mm I. D. x 250 mm) holding at 500°C and then heated in an air stream for 3 min. The evolved gaseous products were introduced to the water, benzene and ethyl alcohol layers in an ice bath. After cooling to room temperature, the reaction tube was rinsed with diethyl ether and this was mixed with diethyl ether extract from the water layer. The combined solvent was then concentrated to 0.1 ml under dry nitrogen gas stream for qualitative and quantitative determinations of PCDDs and related compounds by capillary FID/GC and GC/MS.

Table 1. Polychlorinated alkylphenoxyphenols used for their pyrolysis studies

Name of compound tested	Molecular ion (M <sup>+</sup> )	No. of Cl atoms	Composition (%)	Structural characterization
4-Methyl PCPPs (mixture)	282	2	4	predioxin
	282	2	6	isopredioxin
	316	3	23	isopredioxin
	316	3	19	predioxin
	336	4	1	isopredioxin
	350	4	47	isopredioxin
4-Ethyl PCPPs (mixture)	276	1	2	isopredioxin
	310	2	31	predioxin
	310	2	5	isopredioxin
	344	3	30	predioxin
	316	3	18	isopredioxin
	344	3	10	isopredioxin

## Results and Discussion

Irgasan DP300 has been shown to be converted into 2, 8-dichlorodibenzo-p-dioxin (2, 8-DCDD) upon heating over 300°C (1) and this conversion was also identified to occur in the present work. Higher yield of 2, 8-DCDD from Irgasan DP300 was detected when the compound was heated at 520°C for 3 min in an air stream. At this temperature, high conversion rate (ca., over 80%) to 2, 8-DCDD was observed in the thermo-chemical reactions of original compound. Therefore, this reaction seems to be stoichiometrically.

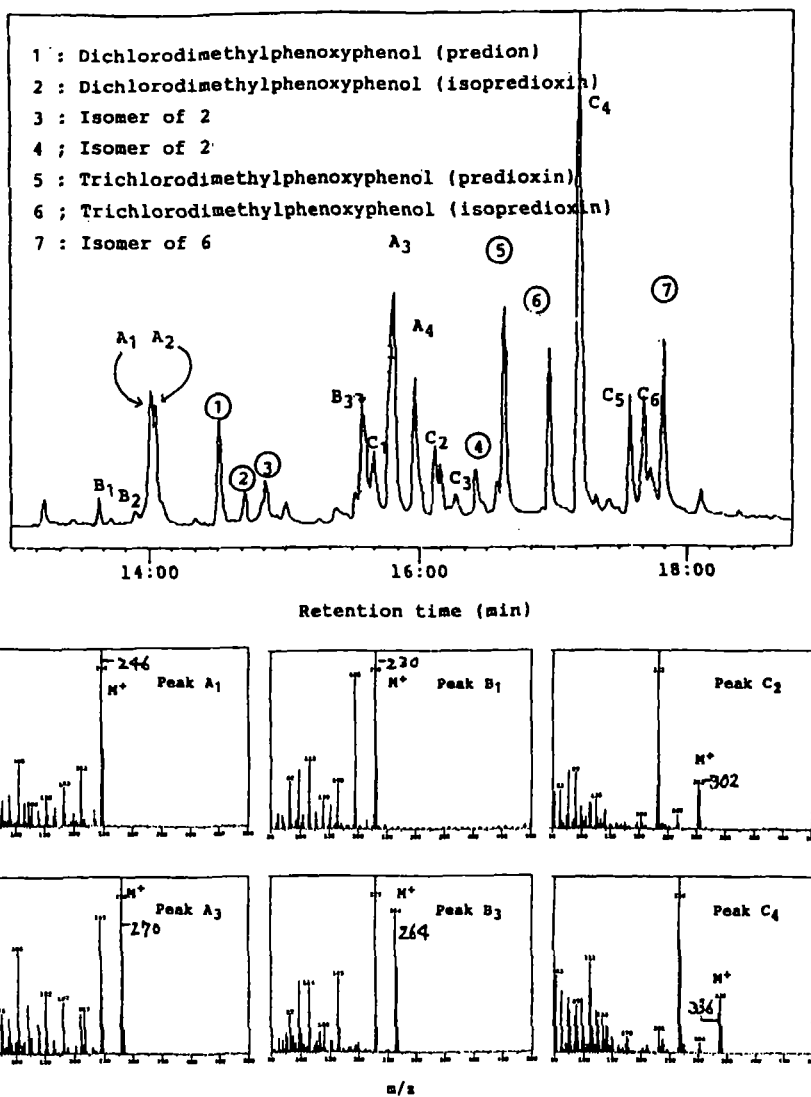


Fig. 1. Mass chromatogram of pyrolysis products of 4-methyl PCPPs mixture in an air stream at 500°C for 3 min and mass spectra of the typical peaks

A typical mass chromatogram (total ion currents) of pyrolysis products of 4-methyl PCPPs mixture in an air stream at 500°C for 3 min and mass spectra of the several peaks are shown in Fig. 1. Except for the original peaks 1 to 7, over 13 peaks including three types of compounds were observed on the chromatogram as pyrolysis products of 4-methyl PCPPs mixture. One of the pyrolysis products corresponding to the peaks A series was methyl PCDDs. The second group corresponding to the peaks B series was methyl DCDFs. The third group corresponding peaks C series was polychlorinated

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monomethylphenoxyphenols.

From the results presented above, it may be concluded that the thermo-chemical reactions of methyl PCPPs in an air stream takes place by the following competing reactions (Chart 1).

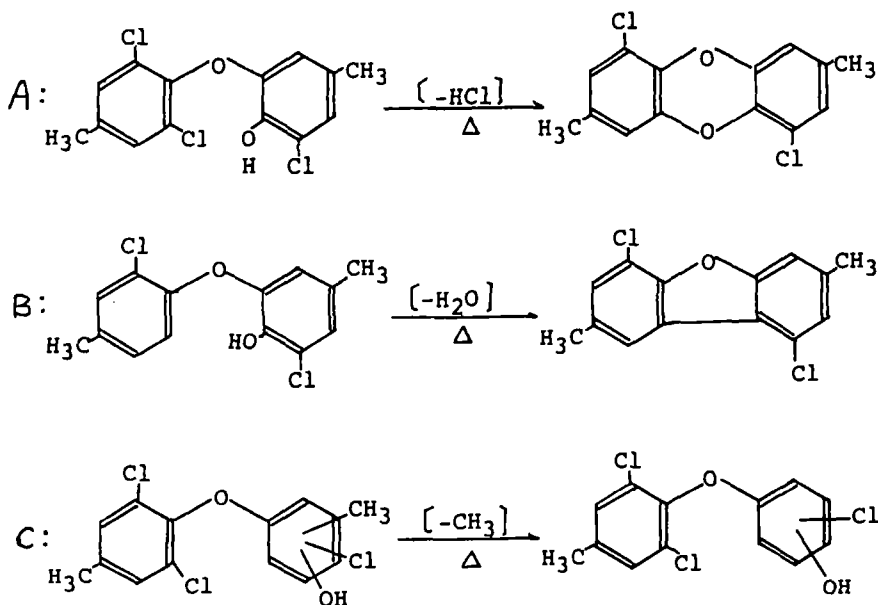


Chart 1. Proposed pathway for thermo-chemical reactions of methyl PCPPs

When 4-ethyl PCPPs mixture was heated at 500°C for 3 min in an air stream, formation of ethyl MCDD and ethyl DCDD was also observed on the chromatogram of its pyrolysis products.

Capillary GC/MS determinations of pyrolysis products of alkyl PCPPs mixtures showed that formation of alkyl PCDDs, alkyl PCDFs and related compounds was observed on heating over 400°C, and higher yields of these compounds were obtained at 550°C and lower levels were obtained at over 650°C.

## Literature Cited

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