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CHROMATOGRAPHIC EVIDENCE FOR THE FORMATION OF CHLORODIOXINS FROM CHLORO-2-PHENOXYPHENOLS

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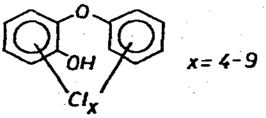
SUMMARY

The photochemical and thermochemical decompositions of a trichloro- and a pentachloro-2-phenoxyphenol have been studied. The photolysis of the pentachloro-2-phenoxyphenol, which is one of the impurities found in commercial 2,4,6-trichlorophenol, gave 1,2,3,8-tetrachlorodioxin, two trichlorodioxins, a dichlorodioxin and a dichlorodibenzofuran. The pyrolysis of the phenoxyphenols yielded a dichloro- and a tetrachloro-dioxin, respectively, as the only detectable products. Consequently, we believe that the level of chloro-2-phenoxyphenols in commercial chlorophenol formulations should be minimized.

INTRODUCTION

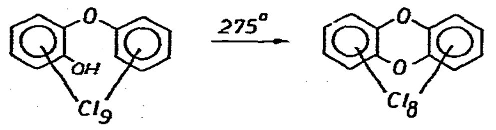
Chlorinated phenols have widespread use as fungicides, bactericides, slimicides, herbicides, etc., and they are also used in the production of phenoxy acids (2,4-D, 2,4,5-T, etc.). The annual world production of chlorinated phenols is approximately 100,000 tons.

Technical formulations of 2,4,6-tri-, 2,3,4,6-tetra- and pentachlorophenol, previously studied in this laboratory, were found to contain dimeric impurities, the main constituents being chlorinated 2-phenoxyphenols with 4–9 chlorine atoms (I)[1-3].



I

Jensen and Renberg[4] arrived at the same result, and subsequently called these compounds predioxins. The nonachloropredioxin II, investigated first, was found to undergo an immediate ring closure to the octachlorodioxin III when analyzed by gas chromatography with the injection block at 275° (refs. 1 and 4).

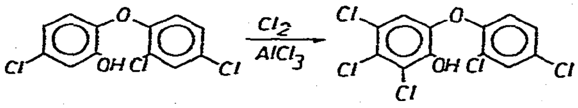


II III

The environmental hazards of chlorodioxins are well known[5], and during recent years a major research effort has been devoted to the examination of many aspects of dioxins. The toxicology of the chlorodioxins has been thoroughly investigated. The maximum activity was found for dioxins with 4–5 chlorine atoms, while lower and higher chlorinated products were found to be much less toxic. For 2,3,7,8-tetrachlorodioxin, the LD_{50} for the guinea pig is reported to be 0.6 μg/kg[6–8].

The discussion of the origin of the dioxins has been focused on two potential sources, namely the amount of dioxins present as impurities in commercial products and the formation of chlorodioxins from chlorophenols by thermal decomposition or irradiation. Until now, no attention has been paid to the possible formation of chlorodioxins from impurities present in chlorophenols or chlorophenoxy acids when they are exposed to environmental conditions.

4,5,6-Trichloro-2-(2,4-dichlorophenoxy)phenol (V) can be prepared in good yield from the chlorination of 5-chloro-2-(2,4-dichlorophenoxy)phenol (IV), which is available as a commercial bactericide known as Irgasan DP 300. Comparison with extracts of commercial formulations of 2,4,6-trichlorophenol showed that V is one of the impurities in this product.

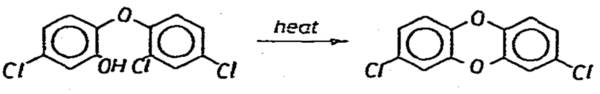


IV V

In this work, we found that both the thermal and the photochemical degradation of the pentachlorophenoxyphenol V yielded 1,2,3,8-tetrachlorodioxin (VI), an isomer that is very similar to the exceptionally toxic 2,3,7,8-tetrachlorodioxin. Poland and Yang[9] found that for highly toxic dioxins, the halogen atoms must occupy at least three of the 2-, 3-, 7- and 8-positions. This requirement is fulfilled by the dioxin VI.

V VI

The corresponding degradation reactions have also been studied for Irgasan (IV). In this instance, only the thermal degradation yielded 2,8-dichlorodioxin (VII).



IV VII

In the identification of these compounds, we used various chromatographic methods in combination with mass spectrometry.

EXPERIMENTAL

Reagents

Methanol (spectroscopic grade), diethyl ether (p.a.), chloroform (p.a.), acetone (p.a.), diazomethane[10], 2,8-dichloro-, 1,2,3,4-tetrachloro- and 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin[9], and 5-chloro-2-(2,4-dichlorophenoxy)phenol (Irgasan DP 300, Ciba-Geigy, Basel, Switzerland) were used.

4,5,6-Trichloro-2-(2,4-dichlorophenoxy)phenol

This compound was prepared by chlorination of Irgasan DP 300 in carbon tetrachloride using aluminium trichloride as catalyst. The yield was 61% of recrystallized pale yellow product, m.p. 100–101°. A detailed description of the preparation and the structure determination will be published elsewhere.

Gas chromatographic system

For the gas chromatographic (GC) runs, a Pye Model 64 instrument equipped with a flame ionization detector (FID) was used. Optimal separation was achieved with a 1.5-m glass column, I.D. 4 mm, filled with 1% OV-17 on 100–120 mesh Diatomite CQ. The operating parameters were: injection block, 275°; column, 200–260°; detector oven, 300°; and nitrogen carrier gas flow-rate, 40 ml/min.

Pyrolyzer system

For the pyrolysis experiments, we used a Pye Curie point pyrolyzer attached to a Pye Model 64 instrument. The column and GC conditions were as above. The wires were cleaned by heating in a micro-flame. After cooling, 2 cm of the wire tips were immersed in a 10% (w/v) solution of the phenoxyphenol in acetone. The wires were dried in air for 30 min and then introduced into the pyrolysis head and pyrolyzed for a period of 15 sec.

Gas chromatographic–mass spectrometric (GC–MS) system

An LKB 9000 mass spectrometer equipped with a Pye Unicam Model 84 gas chromatograph and a split to an FID was used. The column and operating conditions were as above, except that helium at a flow-rate of 30 ml/min was used as carrier gas. The connection between the gas chromatograph and the mass spectrometer was maintained at 220°; additional parameters were: separator, 250°; ion source, 270°, operating at 70 eV.

The GC–MS system was connected with an on line Multi-8 (Intertechnique) computer system (16K bytes core memory) for sampling and processing the mass spectral data.

Photolysis

A solution of 100 mg of the trichloro- or pentachloro-2-phenoxyphenol in methanol (100 ml) was illuminated with a Hanau Q 80 UV lamp ($\lambda_{max.}$ = 290–430 nm, which is close to solar radiation). Aliquots were taken in order to follow the

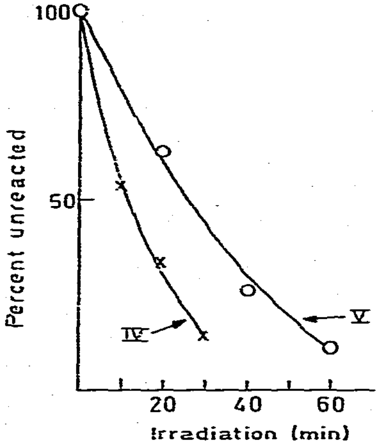


Fig. 1. Decomposition of trichlorophenoxyphenol (IV) and pentachlorophenoxyphenol (V) followed by GC.

photochemical degradation (GC) (Fig. 1). When 10% of the starting phenoxyphenol remained, the irradiation was stopped (30 min for the trichloro- and 60 min for the pentachlorophenoxyphenol). The reaction mixture was carefully evaporated to dryness and the residue dissolved in 10 ml of diethyl ether. Prior to GC–MS analyses and thin-layer chromatographic (TLC) clean-up, a portion of the solution was treated with an ethereal solution of diazomethane.

Thin-layer chromatographic clean-up

A 5 × 20 cm glass plate covered with a 0.25 mm layer of silica gel HF$_{254}$ (nach Stahl) was used, and 200 μl of the untreated ethereal solution were applied as a band with 1,2,3,4,7-pentachlorodioxin as an internal standard. The plate was developed in carbon tetrachloride, and the bands were made visible in UV light. A typical chromatogram is shown in Fig. 2. The dioxin band was scraped off and eluted with 1 ml of acetone. The eluate was carefully evaporated to dryness, and a GC–MS investigation completed the analysis.

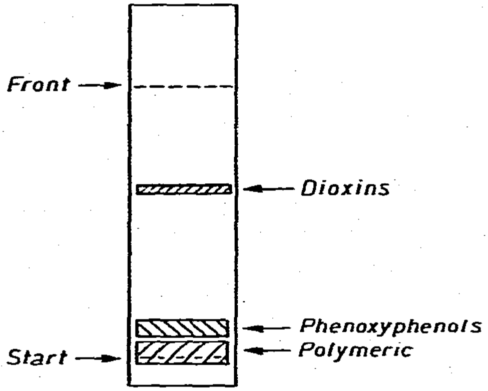


Fig. 2. Thin-layer chromatogram of the photolyzate (60 min) of pentachlorophenoxyphenol (V).

Quantification

In order to determine quantitatively the tetrachlorodioxin formed during the photolysis of the pentachloro-2-phenoxyphenol, an attempt was made using 1,2,3,4-tetrachlorodioxin as an internal standard. However, no satisfactory separation between these two isomers could be achieved on the columns used. In this situation, the relative response between 1,2,3,4,7-pentachlorodioxin and 1,2,3,4-tetrachlorodioxin was determined and the pentachlorodioxin added before the TLC separation, assuming that the two tetrachlorodioxins gave the same response in the FID.

RESULTS

Photochemical degradation

The photolysis of 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol in methanol yielded a large number of products, as can be seen from Fig. 3, which is a chromatogram of the photolyzate. Several of the products could be identified by a comparison of MS data before and after treatment with diazomethane. Peaks 1, 2, 3, 5 and 6 are identified as lower chlorinated 2-phenoxyphenols. This means that the main reaction is a photodechlorination, as has previously been found for polychlorinated biphenyls (PCBs), pentachloronitrobenzene (PCNB) and other halogenated aromatics. Other products identified are chlorinated 2-phenoxyphenols with one methoxy group and hydroxy-PCBs with one or two methoxy groups. A detailed description of this reaction will be given elsewhere.

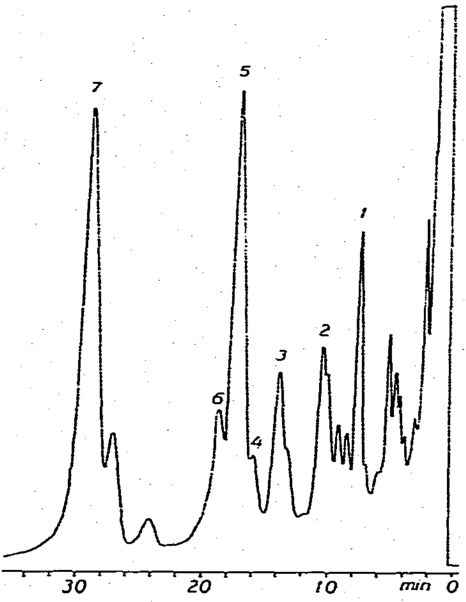


Fig. 3. Gas chromatogram of the photolyzate (60 min) of pentachlorophenoxyphenol (V). Peaks: 1 and 2 = trichlorophenoxyphenols; 4 = tetrachlorodioxin; 3,5 and 6 = tetrachlorophenoxyphenols; 7 = V.

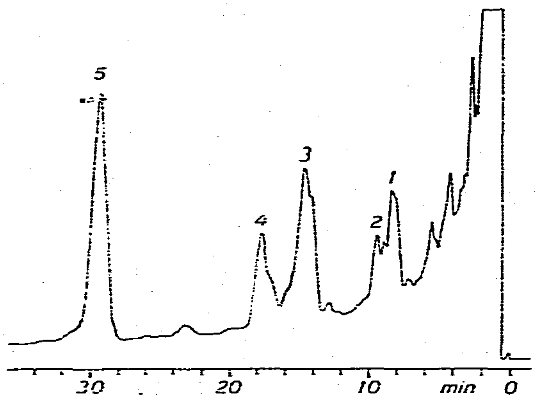


Fig. 4. Gas chromatogram of the dioxin band from TLC clean-up (Fig. 2). Peaks: 1 — dichlorodibenzofuran; 2 — dichlorodioxin; 3 and 4 — trichlorodioxins; 5 — tetrachlorodioxin.

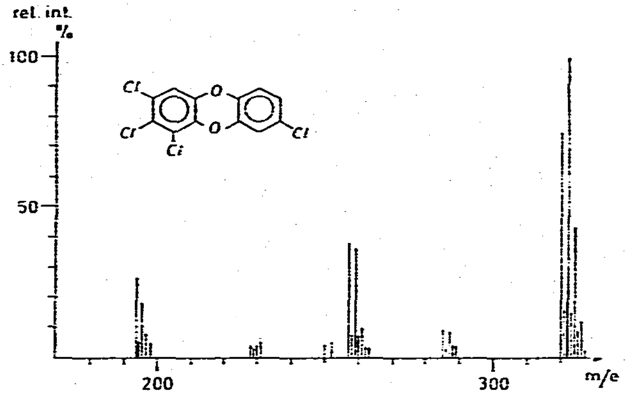


Fig. 5. Mass spectrum of 1,2,3,8-tetrachlorodioxin (VI) (peak 5 in Fig. 4).

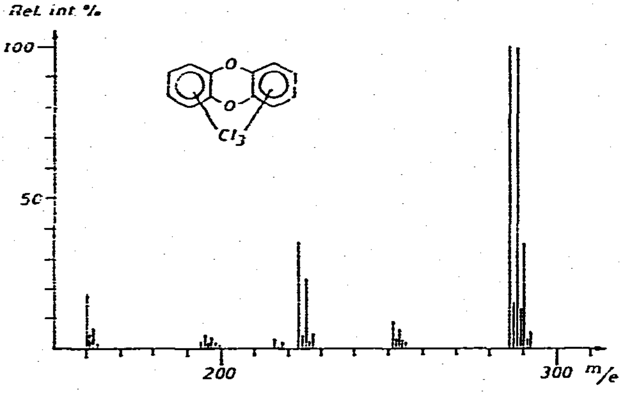


Fig. 6. Mass spectrum of a trichlorodioxin (peak 4 in Fig. 4).

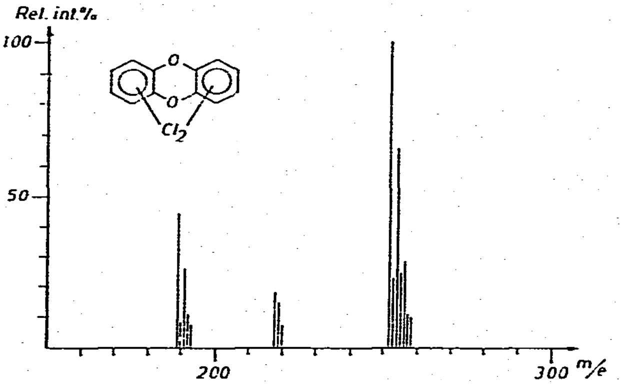


Fig. 7. Mass spectrum of a dichlorodioxin (peak 2 in Fig. 4).

Examination of Fig. 3 shows that the partly resolved peak 4 has a retention time corresponding to a tetrachlorodioxin, and MS gave further support to this assignment.

In this situation, we used a special TLC clean-up[2,4] to separate dioxins (and dibenzofurans) from more polar components such as phenols and phenoxyphenols. The eluate (see Experimental) was analyzed by GC–MS in order to identify the individual components. Fig. 4 is the chromatogram of the eluate from the photolysis of 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol. The mass spectrum of peak 5 is given in Fig. 5, and this peak could be identified as 1,2,3,8-tetrachlorodioxin (VI). The amount of VI was determined to be about 4000 ppm. Peaks 3 and 4 could be identified by MS (Fig. 6) as two isomers of trichlorodioxins, and the sum of these is estimated to be in the 10^3 ppm range. Peak 2 is the dichlorodioxin (Fig. 7) and peak 1 is a dichlorodibenzofuran, the mass spectrum of which is given in Fig. 8. Chlorinated dibenzofurans have been reported to be highly toxic impurities present in PCBs[11].

The photochemical degradation of Irgasan in methanol was found to be faster than the degradation of V (see Fig. 1). The photochemical behaviour of this compound was different, as no dioxin could be observed and the main product in the photol-

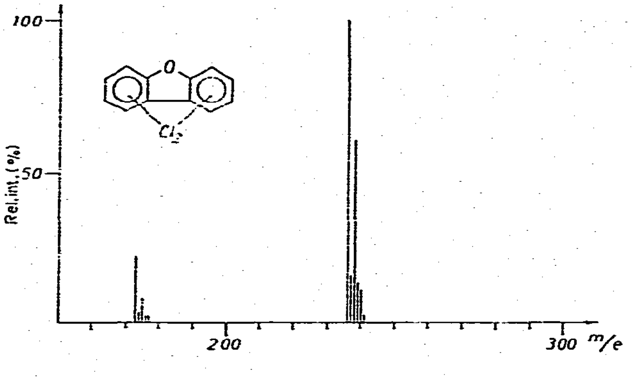


Fig. 8. Mass spectrum of a dichlorodibenzofuran (peak 1 in Fig. 4).

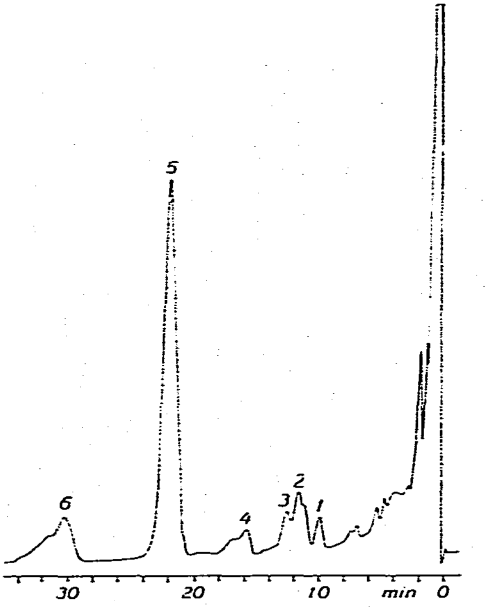


Fig. 9. Gas chromatogram of photolyzate (30 min) of trichlorophenoxyphenol (IV). Peaks: 1 = dichlorodibenzofuran; 2 and 3 = dichlorophenoxyphenols; 5 = IV; 4 and 6 = chlorinated methoxyphenoxyphenols.

yzate was identified as methoxydichlorophenoxyphenol, peak 6 (Fig. 9). Peak 5 is unchanged starting material. The relatively small peaks 2 and 3 are two isomers of dichlorophenoxyphenols. However, this does not exclude photodechlorination from being the main reaction, as it seems likely that dichlorophenoxyphenols decompose even faster than trichlorophenoxyphenol. Peak 1 was identified as a dichlorodibenzofuran.

Thermal degradation

The investigation was performed using a Curie point pyrolyzer unit operating at 358°, 510°, 770° and 980°, attached directly to the column. The chlorinated 2-phenoxyphenols showed unusual stability. At 980°, a temperature at which most organic compounds decompose completely into a large number of fragments, the pyrograms showed only two components (see Fig. 10). The mass spectra revealed that in addition to the starting compounds IV and V, the only compounds formed were the dioxins VI and VII, respectively.

In order to establish the amounts actually pyrolyzed, two needles were used for each pyrolysis experiment. After identical application of substrate, one needle was extracted with 30 μl of acetone in a melting-point capillary tube, while the other needle was first pyrolyzed for 15 sec and then extracted in the same way. By conventional GC analyses of the first acetone solution immediately after the pyrolysis run, the sum of predioxin and dioxin volatilized in the pyrolysis could be estimated as a percentage of initial amount of predioxin. The relative response between the pentachlorophenoxyphenol and 1,2,3,4-tetrachlorodioxin was determined, and the estimation of the

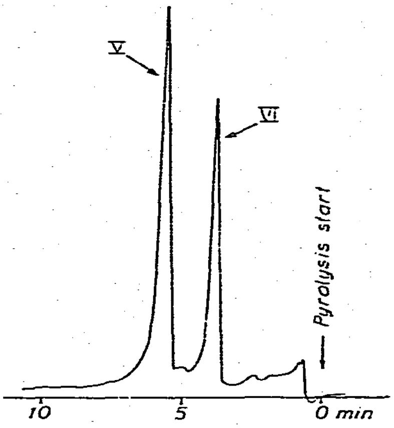


Fig. 10. Pyrogram of pentachlorophenoxyphenol (V). The other peak is 1,2,3,8-tetrachlorodioxin (VI).

1,2,3,8-tetrachlorodioxin formed was (as in the case of photolysis) made assuming that the two tetrachlorodioxins had the same FID response. The acetone extract from the pyrolyzed needle was then injected in order to establish that no volatile compounds remained after the pyrolysis.

In a typical run (770°, 15 sec), it was observed that 70% of the initial pentachlorophenoxyphenol had completely degraded and 30% appeared on the pyrogram as tetrachlorodioxin (3%) and unchanged phenoxyphenol (27%). The results of the pyrolysis at various temperatures are given in Table I. The amount of chlorodioxins was found to increase at higher temperatures, thus the chlorodioxins seem to be even more thermostable than the chlorinated 2-phenoxyphenols.

TABLE I

PYROLYSIS OF CHLORINATED 2-PHENOXYPHENOLS

Temperature (°C)	*Dioxin formed* (%)*	
	Pentachloro-	*Trichloro-*
358	0.4	0
510	0.8	1.7
770	3.0	6.0
980	2.8	6.2

* Calculated on the initial amount of phenoxyphenol.

We also studied the pyrolysis of the potassium salt of V using the same technique. At 770°, the yield of the dioxin VI was approximately ten times higher than that from the pyrolysis of the 2-phenoxyphenol. Contrary to the pyrolysis of 2,4,6-trichlorophenol and its potassium salt, no dioxin (less than 0.1%) could be observed.

DISCUSSION

The photochemical degradation of pesticides and pollutants has been the subject of many recent reports. Crosby *et al.*[12] reported that chlorodioxins decompose rapidly in alcoholic solution and the rate of decomposition increased with a decreasing number of chlorine atoms. The photodecomposition was found to be neglible in aqueous suspensions and on wet or dry soil.

Plimmer and Klingebiel[13] reported that the riboflavin-sensitized photooxidation of 2,4-dichlorophenol gave 4,6-dichloro-2-(2,4-dichlorophenoxy)phenol. However, they did not observe any chlorodioxins. In contrast, the photodecomposition of aqueous alkaline solutions of pentachlorophenol gave a small amount of octachloro- and a heptachlorodioxin[14].

Plimmer *et al.*[14] discussed the formation of chlorodioxins by photochemical reactions from chlorophenols. The rate of formation must be second order in chlorophenols. If consideration is taken of the dilution of chlorophenols and of the high rate at which the lower chlorinated dioxins undergo photolysis, they consider it unlikely that chlorophenols (and chlorophenoxy acids) will form dioxins in the environment. This theory is confirmed by two recent reports by Crosby and Wong[15,16] concerning the photodecomposition of phenoxy acids. However, the situation is completely different when impurities such as chlorinated 2-phenoxyphenols present in commercial chlorophenols are taken into consideration. The formation of chlorinated dioxins from the photolysis of these dimeric compounds is remarkable. The environmental significance of this observation is discussed in the following section.

The thermal decomposition of chlorophenols has been the subject of two reports[17,18]. In some of the experiments carried out by these authors, it was possible to identify small amounts of chlorodioxins, in others not. In all instances, commercial samples were used contaminated with an unknown amount of impurities other than chlorodioxins, *e.g.* chlorinated 2-phenoxyphenols[1-4]. However, chlorodioxins are the main products of the pyrolysis of chlorinated 2-phenoxyphenols, and hence the chlorodioxins observed previously may have been formed more or less exclusively by pyrolysis of the impurities in the commercial samples.

ENVIRONMENTAL SIGNIFICANCE

The annual world production of chlorophenols and chlorophenate is approximately 100,000 tons, and major efforts have been made to minimize the level of dioxins in these products. However, no efforts have been made to minimize the level of chlorinated 2-phenoxyphenols (and their salts). Consequently, this level is 10^3–10^4 times higher than the level of chlorodioxins in many commercial formulations[1-4].

The results reported here clearly show that chlorinated 2-phenoxyphenols are easily metabolized to chlorinated dioxins (and dibenzofurans) under environmental conditions. In the photolysis of V, we estimated the sum of chlorinated dioxins and dibenzofurans to be approximately 1%, and the yield of chlorodioxin from the pyrolysis is significantly higher. The level of chlorinated 2-phenoxyphenols is 1–5%. Thus the amount of chlorodioxins that can potentially be formed in metabolic reactions is significantly higher than the permitted level of chlorodioxins (0.5 ppm). Therefore, the level of chlorinated 2-phenoxyphenols as well as the level of chlorodioxins should be minimized.

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