Meeting Manuscript
Not for Publication

To be presented at the 166th National ACS Meeting, Chicago
August 26-31, 1973

# Photochemical Degradation of PCB

by

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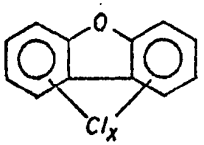
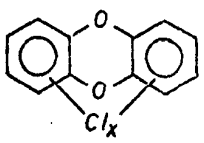
## Introduction

In 1970 it was reported by Vos and coworkers that technical PCB preparations contained small amounts of toxic, polar components, identified by MS as polychlorinated dibenzofurans, 1.[1] From a chemical point of view these chlorodibenzofurans are closely related to the polychlorinated dibenzodioxins (2) known as toxic and teratogenic contaminants in chlorophenols and chlorophenoxy acids.




x = 4,5

1




x = 2-8

2

PCB is known to be stable and resistant to chemical and microbial breakdown. Therefore photochemical degradation may be a major pathway of decomposition.

Gas chromatography is the main analytical method to identify and quantify PCB. A comparison of chromatograms of technical preparations and biological samples shows that some of the main constituents in the technical preparations are lacking in biological samples.[2,3] This would indicate a metabolic breakdown. Holden has proposed that this also can be due to various rates for the photochemical breakdown of different PCB components.[4]

It has been shown in a number of reports that PCB's decompose relatively easily on UV-irradiation.[5-10] In a series of papers Safe and Hutzinger and coworkers have studied the photochemical degradation of technical PCB's and isomerically pure PCB's. They found dechlorination to be the main decomposition pathway, and this has also been confirmed in the other investigations.[6-10] However, in several cases Safe et al.

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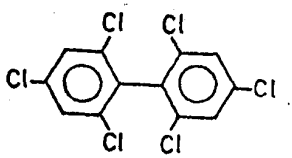
also obtained more polar products containing oxygen, but no real efforts seem to have been made to separate and identify these oxygenated products.[5-7]

Results

We started to investigate the photochemical behaviour of pure 2,2',4,4',6,6'-hexachloro-PCB (3), a PCB previously studied by Safe



3

and Hutzinger.[5] We dissolved 100 mg of 3 in 100 ml of methanol and irradiated the solution for 30 min using a Hanau Q 80 lamp, $\lambda_{max}$ = 366 nm.

The first separation of the variety of products formed was made by TLC, silica gel $GF_{254}$ developed twice with hexane. We could detect at least nine bands, see Fig. 1. Each band was eluated, and the eluate analyzed by means of GC/MS. The chromatograms of bands 5 and 7 are shown in Figs. 2 and 3. We discovered that from this single $Cl_6$-PCB about 80 compounds were formed during the irradiation.

As being reported before[5-10] we found dechlorination to be the main decomposition pathway. We could identify PCB's with 5,4,3,2, and 1 chlorine atom, bands 1-4, Fig. 1. The largest number of products were identified as oxygenated chloroaromatics, in which one or two oxygen atoms have been substituted into the molecule during the irradiation.

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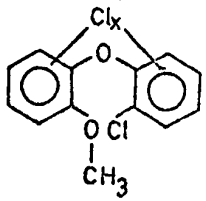
Bands 5 and 6 are not well separated and they were found to contain very similar components. The chromatogram of band 5 is shown in Fig. 2. The dominating peaks are 7,9, and 10. From the mass spectra we could determine the MW to 252, 286, and 320, the mass spectrum of peak 10 is shown in Fig. 3. The MW indicate a series of compounds with 2,3, and 4 chlorine atoms, this was also verified by the chlorine cluster. The compounds all had a typical fragmentation, $M^+ - CH_3Cl$, which also has been found for methylated predioxins (4), compounds with one methoxy and one chlorine in o-positions. From this the conclusion

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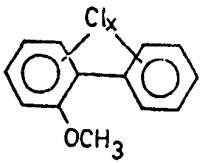


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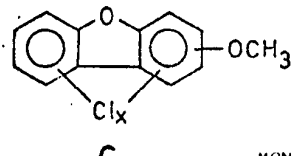
could be drawn that we have a series of o-methoxy-PCB's (5) with 2-4 chlorine atoms. The compound analyzed in peak 10 is the $Cl_4$-compound. The $Cl_1$-compound was found in band 6.

TLC-bands 7,8, and 9 were still more complex, the chromatograms of band 7 is shown in Fig. 5. From this band we could identify two series of compounds with increasing amount of chlorine atoms, one MW 232 ($Cl_1$) and 266 ($Cl_2$) and the other MW 216 ($Cl_1$), 250 ($Cl_2$), and 284 ($Cl_3$). In Fig. 3 is given the spectrum of the compound MW 266, which we consider to be a dichloromethoxydibenzofuran, 6, x=2.

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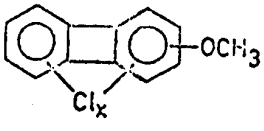
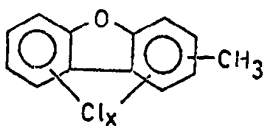
The structure of the other series in band 7 is still unclear, chlorinated methoxybiphenylenes (7) or methyldibenzofurans (8) are both possible.




7

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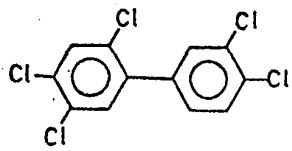
Bands 8 and 9 were identified as products with two oxygen atoms. The structure of these compounds is still unclear, but in Fig. 1 we have given some suggestions.

We have expanded our investigation to include 2,3',4,4',5-pentachloro-PCB, 9. This isomer is one of the main components in technical PCB, which is not present in some biological samples.[13] In this PCB only one of the o-positions has a chlorine substituent.

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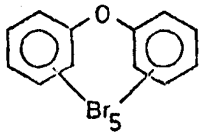
The $Cl_5$-PCB 2 was irradiated and analysed as described above for the $Cl_6$-compound, the TLC is visualised in Fig. 5. In addition to starting material and dechlorination products (Bands 1-3) only one band can be detected. GC/MC analyses showed that the main constituent in this band is $Cl_4$-o-methoxy-PCB 5. The lower chlorinated analogues could also be detected, but to much smaller amount. From our investigation the conclusion could be drawn that the photochemical degradation of the $Cl_5$-PCB 2 does not yeld any detectable amounts of fused system of dibenzofuran type like 6 and 8 or diphenylene type (7). This type of photometabolites can only be formed from PCB's having at least one o-chlorine and one o'-chlorine. However, this substitution pattern is very common for components in commercial PCB's.[14]

## Toxicological test

No information concerning the toxic, genetic, cancerogenic or teratogenic effects of the identified photometabolites is available from the current literature. A preliminary toxicity test was performed using Drosophila melanogaster, stock KÄS. The evaporated eluate from the TLC-bands 5 + 6 and 7 from the photolysis of $Cl_6$ - PCB was added with the feed and the results are collected in Table 1.
Examination of this table reveals that the oxygenated photometabolites of PCB show a pronounced increase in toxicity compared to the starting material, the $Cl_6$-PCB. It can be noted that for the dose 0.1 ppm the toxicity of these photometabolites is about the same or higher than the toxicity of the insecticides aldrin and lindan.

In this toxicity test we have also included a commercial flame retendant, Bromkal 70, which is pentabromodifenylether (10). Compared to $Cl_6$-PCB this product showed an increased toxicity.



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Conclusion

We have found that oxygenated photometabolic of PCB are much more toxic than PCB. This means that if PCB should be destructed by photochemical reactions, the conditions must be chosen to avoid any formation of oxygenated products. The environmental fate of PCB must be carefully investigated. We feel that special interest must be devoted to the photochemical degradation of PCB in air, in water, and on surfaces.

Moilanen and Crosby reported before the 165th national ACS meeting at Dallas in April this year that DDT vapor can be converted to PCB's by a photochemical process. Special attention should be devoted to the degradation of the PCB isomers formed in this process.

Recent reports concerning the metabolism of PCB's show that PCB's are metabolized to hydroxy-PCB's.[16,17] Our result indicate that the metabolites could be more toxic than PCB.

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Table 1

| Compound | Dose ppm | % Animals dead after 4 days |
|---|---|---|
| | 10 | 4[a] |
| $Cl_6$-PCB (3) | 50 | 12 |
| | 100 | 49 |
| "Band 5+6" | 0,1 | 44 |
| $CH_3O$-PCB's | 1 | 64 |
| | 10 | 42 |
| "Band 7" | 0,1 | 55 |
| | 1 | 81 |
| | 10 | 55 |
| Bromkal 70 (10) | 0,1 | 32 |
| | 1 | 41 |
| | 10 | 23 |
| Aldrin | 0,1 | 12 |
| | 1 | 97 |
| | 10 | 100 |
| Lindan | 0,1 | 19 |
| | 1 | 27 |
| | 10 | 100 |

a) obtained after 2 days

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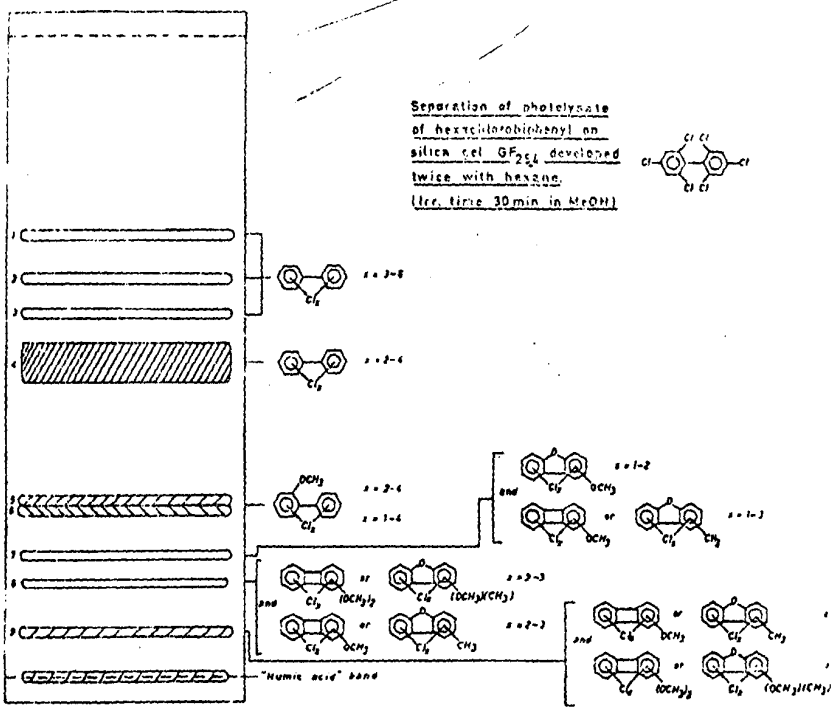
Separation of photolysate of hexachlorobiphenyl on silica gel $GF_{254}$ developed twice with hexane (Rf, time 30 min in MeOH)
"Humic acid" band
and
or

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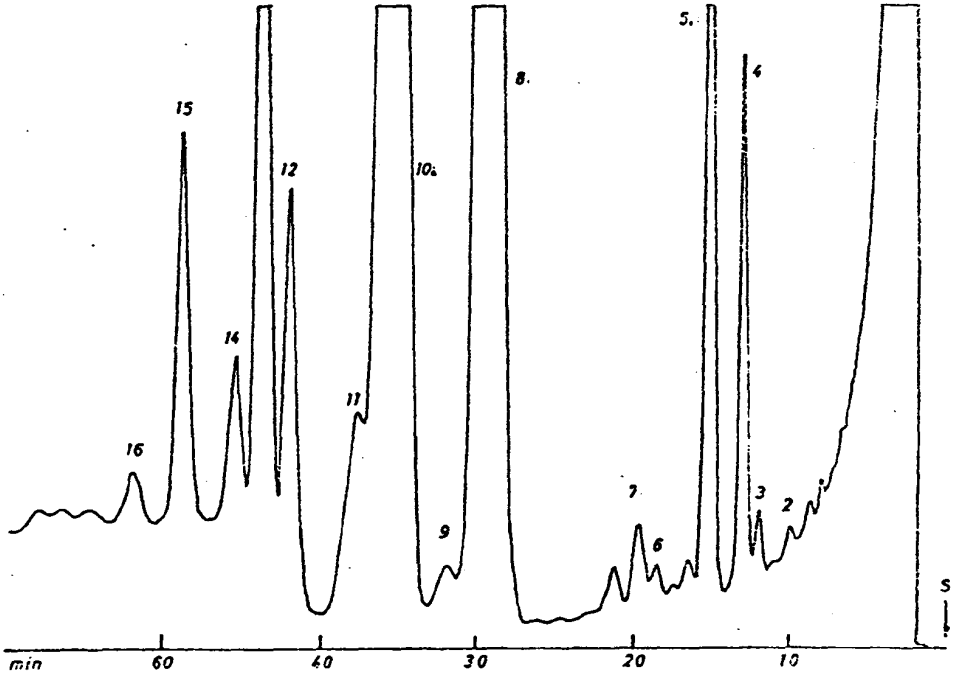
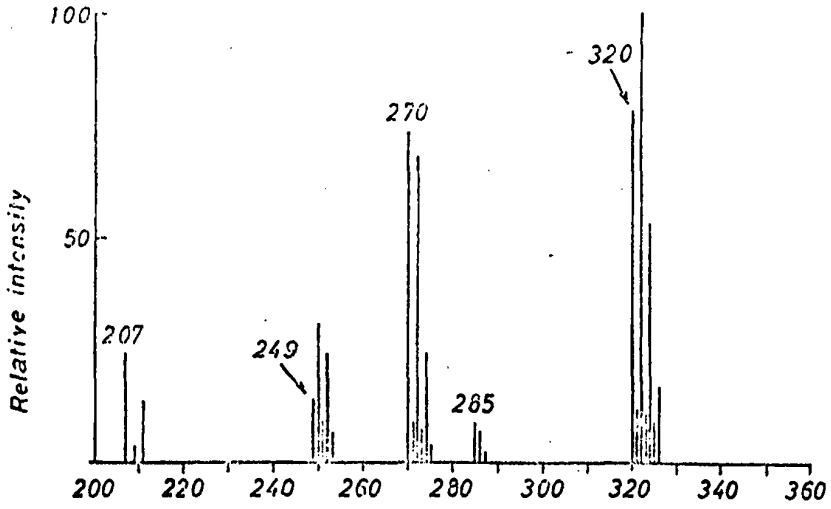
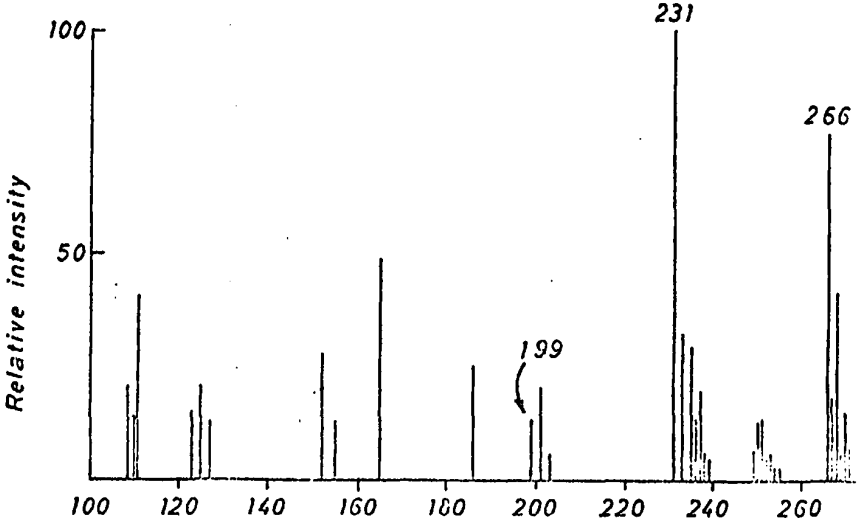



*Chromatogram of "TLC band 7" obtained during GS-MS run. GC conditions as before but temp. raised after 40 min.*




Mass spectrum of peak no 10 from "TLC band 5"




Mass spectrum of peak no 14 from "TLC band 7"

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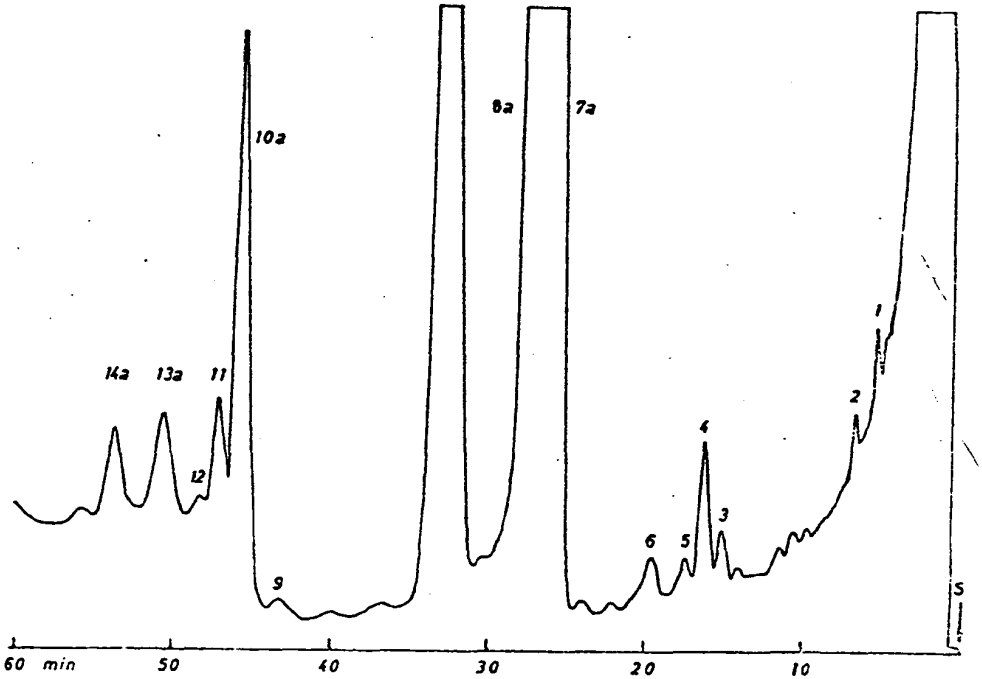
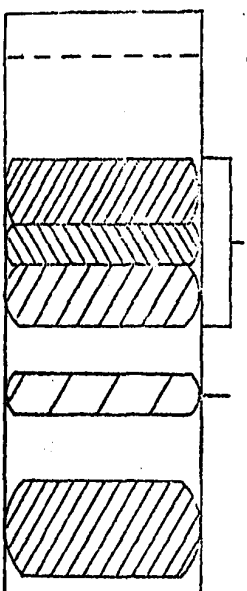
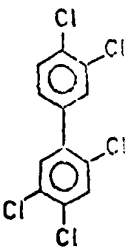
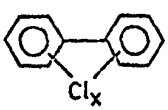



Chromatogram of "TLC band 5" obtained during GC-MS run.
Column: 2.1 m 1% APM, oven temperature 190° isothermal, after 45 min raised to 220° C.
a) Peaks identified as methoxysubstituted PCBs.

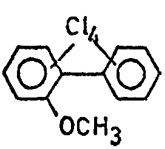


Separation of photolysate of pentachlorobiphenyl on silicagel $GF_{254}$ developed twice with hexane. (Irr. time 30 min in MeOH)




x = 2-5




"Humic acid" band