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NATIONAL INSTITUTE OF
ENVIRONMENTAL HEALTH SCIENCES
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RECEIVED

JAN 29 1979

J. F. BROWN JR.

Dr. John F. Brown
Manager, Life Science Branch
Physical Chemistry Laboratory
Building K1, Room 3835
General Electric Company
Research & Development Center
Post Office Box 8
Schenectady, New York 12301

Dear Dr. Brown:

It is obvious to me at this point that we are not communicating. Perhaps I have assumed a greater appreciation and understanding of the problems and difficulties involved than you and your staff may have at this time. However, I will briefly address the questions raised in your letter of January 15, 1979, and then suggest some alternatives to communicating this matter.

1. Furan Nominal Mass Equivalents. We now know that there is a series of these "furan like" (mass spectrometrically similar but chromatographically different) compounds in the used transformer fluid also. They are found in the fraction most enriched in chlorinated diphenylethers off acidic alumina. More fluid (new and used) will have to be processed in order to obtain sufficient quantities of these fractions for further study. We plan to obtain exact mass measurements pending availability of proper fractions and instrument time.

2. Model Conditions for Furan Formation. I have enclosed a preprint of an article describing some additional work in this area. These workers claim that the furans can be formed at temperatures as low as 270° for one week. I will not attempt to extrapolate that to the transformer situation. My surprise was in not having been able to find detectable levels of furans. Appreciable levels would not be expected in view of the possible competing reaction leading to diphenylethers. Without starting over, all we can say at the moment is that if the furans are present they are <100 ppm.

3. Identification of Hydrocarbons. It was not our intent to elaborate the identification of minor components at this time. However, our identifications are generally based on two or more of the following criteria: proper chromatographic behavior, proper molecular ion including isotopic ratios, and expected fragmentation. Although the identifications are not generally considered definite, they are not based on molecular ions alone. In the case of C₁₆H₃₄ hydrocarbon which is a major component among the

minor ones, we have an exact mass measurement as confirming evidence. In addition, it is not surprising for a compound such as this in such a complex mixture to overlap with several fractions. The latter speaks for our experience in this area.

4. Identification of Chlorinated Diphenylethers. There is no question about this one. All of the following is consistent with this identification: chromatographic behavior under diverse conditions, mass spectral patterns including parent ions, diagnostic fragments such as $M-COCl$, and isotopic ratios, perchlorination to decachlorodiphenylether, and UV-absorbance. We also have representative standards. In fact, we now know that the chlorinated diphenylethers constitute approximately 8 mol. percent or 11 wt. percent of the used transformer fluid. Chlorinated bi-phenylols will silylate, you just have to use the right silylating conditions. Also, the diphenylethers have some water solubility, hence their presence in the aqueous basic solution is expected since there is very little of anything else to compete for water solubility.

5. Origin of "Used" Transformer Fluid. I find it very disturbing that the identification of this fluid as originally stated was incorrect. This is the one area for which we had hoped we could rely on you, as a definitive history of the sample is critical to any publication of this work.

We agreed and continued to work with this fluid because it offered a peculiar challenge to a separations group. Our purpose and approach to this study was purely scientific; however, we did hope to publish our findings as we should. In fact, we now feel we have a general scheme for any future analysis of such fluids which utilizes a combination of UV-monitoring, chromatography and perchlorination techniques to avoid arbitrary "cuts" and solvent changes, etc.

In short, we have researched the methodology while trying to provide you some answers. Obviously, there is some risk involved in doing this, but the urgency and need were there, and we have the expertise. I will not continue to send raw data and our interpretation as I have done in the past, for it only seems to get taken out of context. This is really not practical anyway as we have reams of data on the subject now. Rather, I would suggest that you visit with us so that we can lay out our data and talk about it some in detail. On the other hand, if you will provide a sample of used transformer fluid of known origin and usage, which would not seem to be a formidable task for GE, we will apply our methods and publish our data for the scientific community to evaluate. Of course, another alternative is for you to do the work yourself; however, if you choose to do this, I think it will require a great deal more appreciation of the problems and difficulties involved and familiarization with metho-

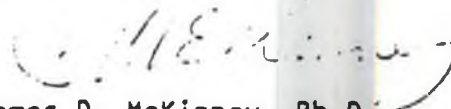
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dologies than apparently you have at the moment (as least as conveyed in your letters on the subject).

Sincerely,



James D. McKinney, Ph.D.
Chief, Environmental Chemistry Branch

Enclosures 1

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POLYCHLORINATED DIBENZOFURAN(PCDF) FORMATION FROM
PCB MIXTURE BY HEAT AND OXYGEN

By

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Bull Environ Contam Toxicol

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Polychlorinated dibenzofurans(PCDFs) are known highly toxic compounds (HOFMANN,1958). Like their close chlorodibenzodioxin analogues, certain of the PCDF compounds are extremely toxic to mammals, causing chloracne and producing extensive, irreversible liver damage (KIMBROUGH 1972, TAYLOR 1974). PCDFs are also extremely toxic to chicks (MCKINNEY et al. 1976). Recently PCDFs are considered to have played a significant role in the causation of "Yusho" to which PCB mixture(Kanechlor 400)have been found responsible (NAGAYAMA et al. 1976).

The PCDF derivatives have been detected and identified in manufactured polychlorophenols (NILSSON and RENBERG 1974; BUSER 1975) and in PCB preparations of various source (VOS et al. 1970; ROACH and POMERANTZ 1974; BOWES et al. 1975, 1976; MORITA et al. 1977). From the structural similarity, the possibility of PCDF formation from a PCB source was an item of special interest. The photochemical transformation has been studied in several reports (SAFE and HUTZINGER 1971; HUTZINGER et al. 1972; ANDERSON et al. 1975). There is also some evidence that PCDFs may be produced thermochemically. PCB mixture used at high temperature as a heat transfer agent were shown to have an increased amount of PCDFs (MORITA et al. 1977). In Yusho oil an unusually high level of PCDFs was considered as a result of a long term heating of PCBs for heat transfer use. These indication led us to heating experiments to learn

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necessary conditions, yield and mechanism of the reaction. We here present a preliminary result of our heating experiments of an American PCB mixture (Arochlor 1248).

EXPERIMENTAL

PCB mixture (Arochlor 1248, 1g) was sealed with air, oxygen or nitrogen in pyrex glass tube (8mm X 200mm) and heated in an oven. After cooled to room temperature, the content was dissolved with 10 ml of n-hexane and vigorously shaken with pellets of sodium hydroxide.

Half of the solution was subjected to PCDF analysis.

Clean up procedure was similar to that described by MIYATA et al.. Aluminium oxide (Merck Aluminium Oxid 90 aktiv, 27g) was packed in a glass column (10mm X 300mm) with hexane (Mallinkrot nanograde). PCBs were eluted with 200ml of dichloromethane+hexane mixture (5:95) and then with 50ml of 20% dichloromethane mixture. PCDFs were recovered with 250 ml of dichloromethane+hexane (20:80) mixture. The PCDF fraction was concentrated to the volume of 1 ml with a Kuderna-Danish concentrator and then nitrogen gas flashing. An aliquot of the solution was injected to gaschromatography-mass spectrometer (Shimadzu LKB9000) for quantitative and qualitative analyses. The amount of PCDFs were determined by comparing the peak areas of parent mass chromatogram with those of authentic PCDF mixtures assuming that the sensitivity of total ion collector is the same among PCDF isomers regardless to the difference of chlorine position and number. GC conditions was as follows. Column OV-210 (2%) on Chromosorb WAW DCMS (100/120). Carrier gas He 30 ml/min.

RESULTS AND DISCUSSION

Three parameters, heating temperature, oxygen

partial pressure and time, were studied for the formation of PCDFs. As shown in Fig.1 and 2, the conditions were critical. The maximum yield in this experiments was about 0.2 %.

Heating PCBs for 1 week showed that PCDFs were formed over about 270°C and reached to the maximum level at about 300°C (in oxygen). The lower level at 330°C may suggest that PCDFs were decomposed at this temperature in oxygen. On the other hand, higher temperature seems necessary for the PCDF formation. No significant increase of PCDFs was observed in the heating at 270°C and higher yield was obtained at 330°C rather than at 300°C. A very slight increase of PCDFs was noticed in the heated PCBs at 330°C under nitrogen.

Fig. 2 shows the effect of time when PCBs were heated at 300°C. Under oxygen, the maximum was found after 1 week while it was found after 2 weeks in air. Prolonged heating decreased the PCDFs level indicating that once formed the PCDFs were decomposed under these conditions. Very slight increase of the PCDF level was observed in long term experiments heating PCBs under nitrogen.

From these observations, the reaction may be delineated by the following description.

(1) Oxygen atom in PCDF skelton comes from oxygen gaseous in the sealed tube.

(2) Temperature over 270°C is necessary for the transformation but at temperature over 330°C PCDFs decomposes.

(3) PCDFs level seems to be determined by the transient equilibrium of thermal formation and decomposition and thus gives a critical point for heating conditions.

(4) Slight formation of PCDFs under nitrogen may be due to oxygen gas impurities or the effect of water or some other impurities absorbed on the glass surface.

Fig. 1

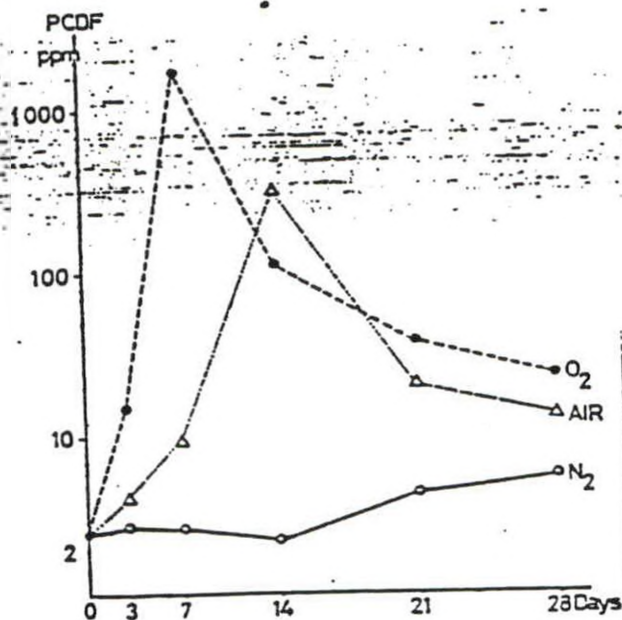


Fig. 2

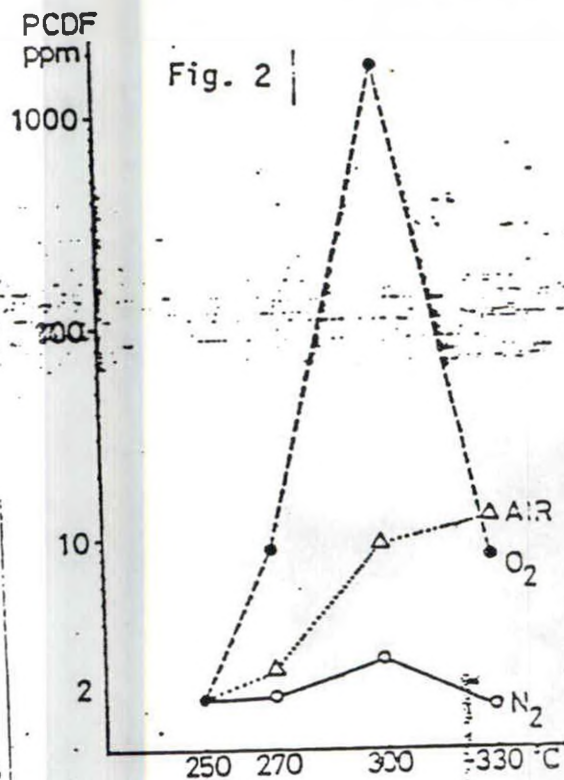
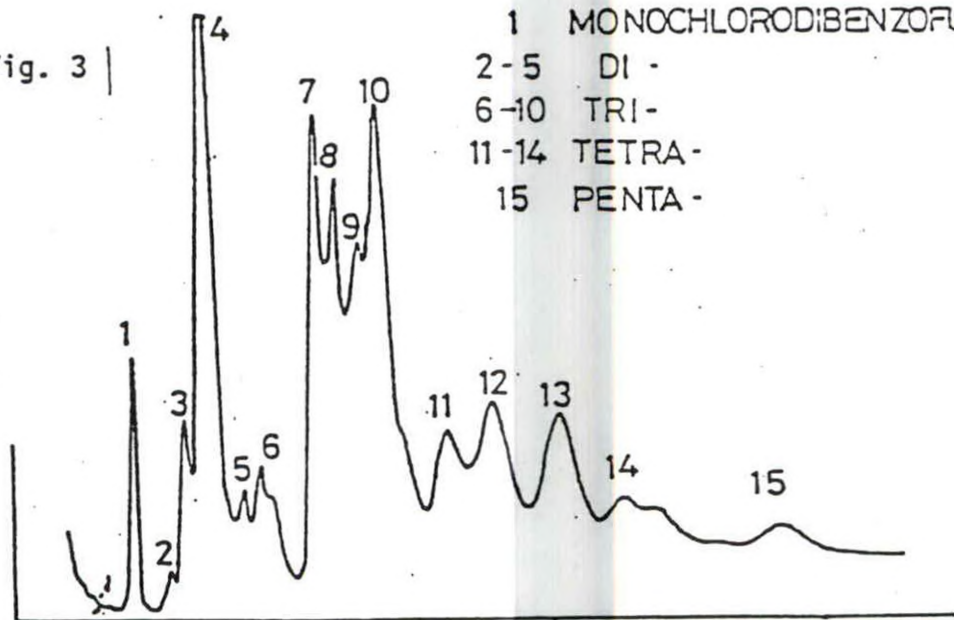


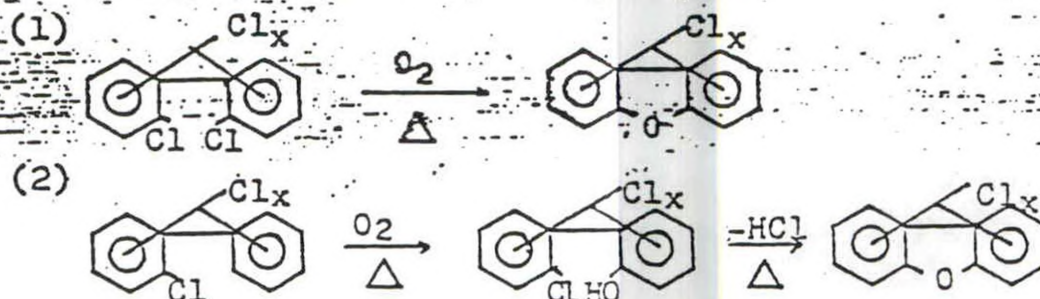
Fig. 3



- 1 MONOCHLORODIBENZOFURAN
- 2-5 DI -
- 6-10 TRI -
- 11-14 TETRA -
- 15 PENTA -

GASCHROMATIC PATTERN OF PCDF IN HEATED PCB
(300°C. in O₂ , 1 Week)

Fig. 3 shows the gaschromatogram of PCDFs in heated PCBs at 300 C under oxygen for 1 week. Major components were dichloro and trichlorodibenzofurans. Since major components of starting PCB mixture (Arochlor 1248) was tetrachlorobiphenyls, it is apparent that one or two chlorine atoms were released in the reaction. Therefore the following mechanism may be speculated.



Similar mechanisms are discussed in the earlier report on the PCDF formation during Ullman reaction for PCB synthesis (MORITA et al. 1977).

In analogy to the chlorodibenzodioxins, the toxicity of PCDFs is supposed to be structure highly dependent as to the position and number of chlorines: 2,3,7,8-tetrachlorodibenzofuran might be the isomer of the highest toxicity. Peak no. 15 was confirmed to correspond to 2,3,7,8-tetrachlorodibenzofuran by co-injection technique. The level was c.a. 80ppm in the sample analyzed in Fig.3. It was noteworthy that the extremely toxic 2,3,7,8-TCDF was formed in heated PCBs.

Yusho oil contained an increased amount of PCDF isomers but the isomer components were quite different from those obtained here. Major components in Yusho oil were tetra- and pentachlorodibenzofurans while those obtained here were di- and trichlorodibenzofurans in spite that the starting PCBs were supposed to be similar in their chlorine content. Therefore other reaction mechanisms or subsequent reactions might be considered for the formation of PCDFs in Yusho oil. Heated metal tubings might be responsible to the difference.