Bull. Environm. Contam. Toxicol. 19, 665-670 (1978)

Polychlorinated Dibenzofuran (PCDF) Formation From PCB Mixture by Heat and Oxygen

M. Morita[1], J. Nakagawa[1] and C. Rappe[2]
[1]*Tokyo Metropolitan Research Laboratory of Public Health, 3-24-1, Hyakunin-cho, Shinjuku-ku Tokyo, 160 Japan,* [2]*University of Umea, S-901 87 Umea 6, Sweden*

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 posibility of PCDF formatin 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

---

Any correspondence be addressed to M. Morita,Ph.D.

0007-4861/78/0019-0665 $01.20

necessary conditions, yield and the 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 analuses. 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 equibrium 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

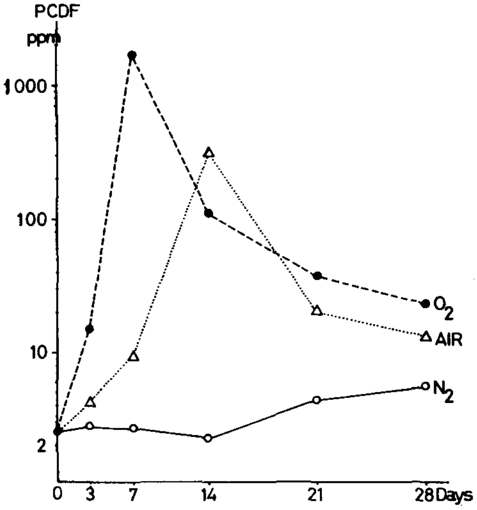


Fig. 2

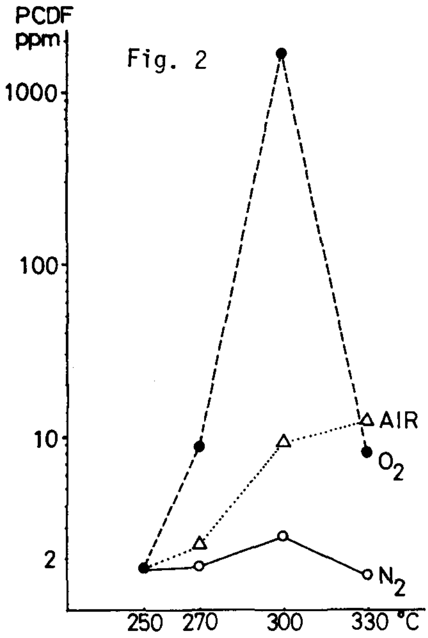
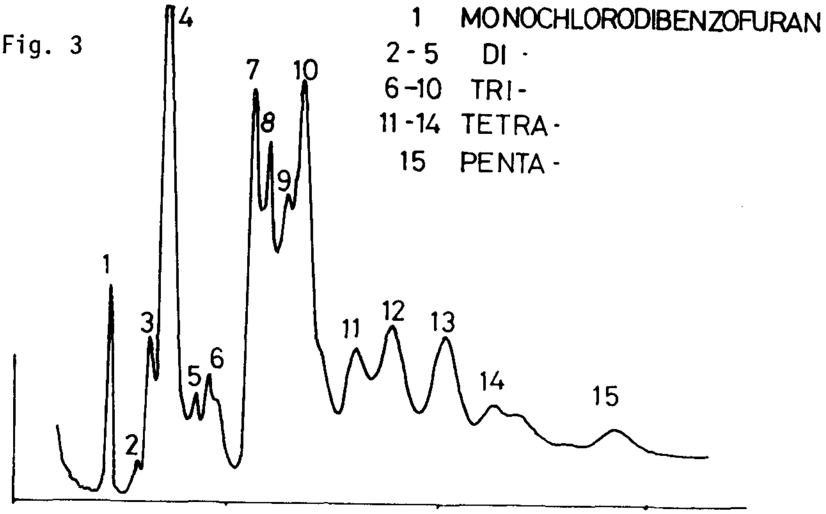


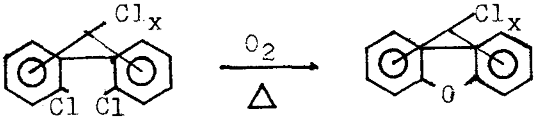
Fig. 3



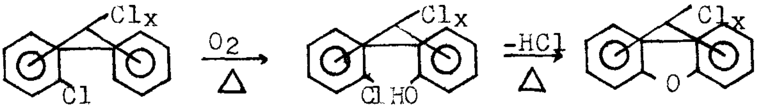
GASCHROMATIC PATTERN OF PCDF IN HEATED PCB (300°C, in O_2, 1 Week)

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.

(1)



(2)



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 tecnique. 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.

REFERENCES

ANDERSSON,K., NORSTROM,A., RAPPE,C., RASMUSON,B. and SWAHLIN,H. : Environmental Quality and Safety, 798(1975)

BOWES,G.W., MULVIHILL,M.J.,DECAMP,M.R. and KENDA,A.S. : J. Agric. Food Chem.

BOWES,G.W., MULVIHILL,M.J., SIMONEIT,B.R.T., BURLINGAME, A.L. and RISEBROUGH,R.W. :Nature 256, 305 (1975)

BUSER,H.R. : J. Chromatogr. 107, 295 (1975)

HOFMANN,H.TH. : Arch. Exp. Path. Pharmak. 232, 228(1958)

HUTZINGER,O., SAFE,S. and ZITKO,V. : Environ. Health Perspect. 1, 15 (1972)

KIMBROUGH,R.D. : Arch. Environ. Health. 25, 125 (1972)

MCKINNEY,J.D., CHAE,K., GUPTA,B.N., MOORE,J.A. and GOLDSTEIN,J.A. : Toxicol. Appl. Pharmacol., 36, 65(1976)

MORITA,M., NAKAGAWA,J., AKIYAMA,K., MIMURA,S. and ISONO, N. : Bull Environ. Contam. Toxicol. in press.

MORITA,M., NAKAGAWA,J. and AKIYAMA,K. : Bull. Environ. Contam. Toxicol. in press.

NAGAYAMA,J., KURATSUNE,M. and MASUDA,Y. : Bull. Environ. Contam. Toxicol. 15, 9 (1976)

NILSSON,C.A. and RENBERG,L. : J. Chromatogr., 89, 325 (1974)

ROACH,J.A.G. and POMERANTZ,I.H. :Bull. Environ. Contam. Toxicol., 12, 338 (1974)

SAFE,S. and HUTZINGER,O. : Nature, 232, 641 (1971)

TAYLOR,T.S. : Cutis, 13, 585 (1974)

VOS,J.G., KOEMAN,J.H., van der MAAS,H.L., ten NOEVER de BRAUW,M.C. and de VOS,R.H. : Food Cosmet. Toxicol., 8, 625 (1970)