Photochemical Degradation of Isomerically Pure Di-, Tetra-, Hexa-, Octa- and Decachlorobiphenyls

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We have previously shown that photochemical changes occur in chlorinated biphenyls on irradiation with a number of light sources (1,2). This report deals with the behaviour of a number of chlorobiphenyls on exposure to natural sunlight.

Experimental

100 Milligrams each of 4,4'-dichlorobiphenyl (I), 3,3',4,4'-tetrachlorobiphenyl (II), 2,2',5,5'-tetrachlorobiphenyl (III) and 2,2',4,4',5,5'-hexachlorobiphenyl (IV) were dissolved in benzene and spread evenly on a pyrex dish (diameter: 35 cm) under a gentle flow of air to ensure uniform formation of a chlorobiphenyl film. Distilled water (5 ml) was added to the dishes which were then loosely covered with plastic material to prevent dust and rain to contaminate the chlorobiphenyl film but allow air to exchange. Dishes were exposed, on the laboratory roof, for the period June 24 to September 15, 1971. Total duration of bright sunshine was 612 hours (4).

After this period of exposure the contents of the dishes were dissolved in acetone and the solvent and residual water removed by evaporation. After weighing, the residue was redissolved in each case, streaked onto a preparative TLC plate (20 × 100 cm coated silica gel F-254) and the plate developed in hexane three times. Three bands were visible on the plates under U.V. illumination: band A at R_f 0.7-0.9 corresponding to the starting material; band B at R_f 0.4-0.7 which was usually weak and band C at the origin to approximately R_f 0.1. The bands were eluted with benzene-ethyl acetate (A,B) and ethyl acetate-acetone (C) with the addition of small amounts of water, the solvent removed and the crude extracts examined by mass spectrometry using a DuPont/CEC 21-110B double focussing instrument. The samples were slowly heated in the direct introduction probe and electrical scans as well as photoplate exposures obtained at different temperatures.

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Results and Discussion

The main conclusions for the behaviour of the four compounds on exposure to natural sunlight (see table) are as follows:

(a) Loss of weight occurred presumably by evaporation of either the starting material or more volatile breakdown products. The amount of crude material recovered from the dishes was 4.8 mg (I); 7 mg (II); 17 mg (III) and 34 mg (IV). Future experiments will be conducted in closed quartz tubes.

(b) Contrary to irradiations in hexane where stepwise loss of chlorine was observed, irradiations in thin films produces chlorobiphenyls of higher chlorine content. In this case the substrate probably acts as scavenger ("solvent") for the Cl· produced. Under the present experimental conditions, however, extensive loss of compounds with lower vapour pressure (chlorobiphenyls containing less chlorine) is likely.

(c) A band corresponding to more polar products was observed on TLC in all cases. Mass spectra for definite compounds containing chlorine could not be obtained, however, which indicates the products to be either polymers or thermally labile compounds with little or no chlorine remaining.

(d) A number of peaks corresponding to chlorinated compounds other than PCB were observed. Among these were terphenyls and compounds whose compositions could not be deduced from the low resolution spectra. High resolution data from the photoplates are being processed. These data and information on other isomers will be available.

References

1. S. Safe and O. Hutzinger, Nature, 232, 641 (1971).
2. O. Hutzinger, S. Safe and V. Zitko, Environmental Health Perspectives, 1, in press (1972).
3. D. G. Crosby and M. Y. Li, "Herbicide Photodecomposition" in "Degradation of Herbicides" (ed. P. C. Kearney and D. D. Kaufman), M. Dekker Inc., N. Y.; 1969; p. 321.
4. Values from Canadian Force Base Shearwater, Halifax Co., N. S., supplied by Maritimes Weather Office, Atmospheric Environment Service.

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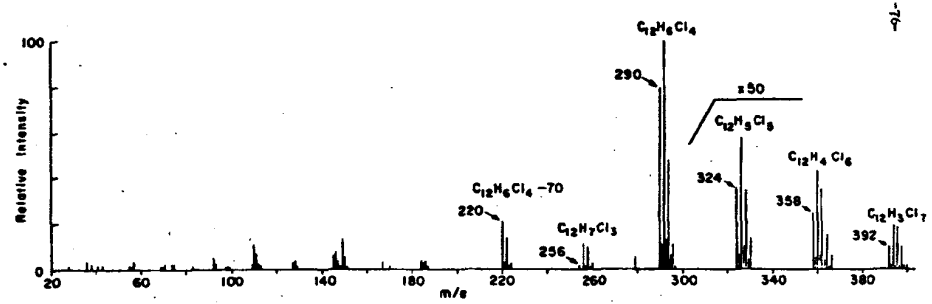

Figure 1. Mass spectrum of "TLC band A" from 3,3',4,4'-tetrachlorobiphenyl exposed to sunlight.

Mass Spectr

Band I

A Cl
trace
Cl_3,C

B m/e 4
509,

C +
and methylated

Legend: + = Many peak
impuritic
apparent.
Cl_4, Cl_5, etc

TABLE

Mass Spectral Data on Compounds Formed by Irradiation

Band	Chlorobiphenyl irradiated			
	I	II	III	IV
A	Cl_2 trace Cl_4, Cl_5, Cl_6	Cl_3, Cl_4, Cl_5, Cl_6, Cl_7 (Fig. 1)	Cl_4, Cl_5, Cl_6, Cl_7	+
B	m/e 476, 509, 542	Chloroterphenyls (Fig. 2) trace Cl_4, Cl_8	-	m/e 248, 284, 320, 354, 412, 446, 480, 574 (Fig. 3) Different minor peaks at different probe temperatures
C and methylated	+	+	+	+

Legend: + = Many peaks due to either extensive decomposition of samples or impurities; no pattern characteristic for chlorine isotopes apparent.

Cl_4, Cl_5, etc. = tetra-pentachlorobiphenyl, etc.

Figure 1. Mass spectrum of "TLC band A" from 3,3',4,4'-tetrachlorobiphenyl exposed to sunlight.

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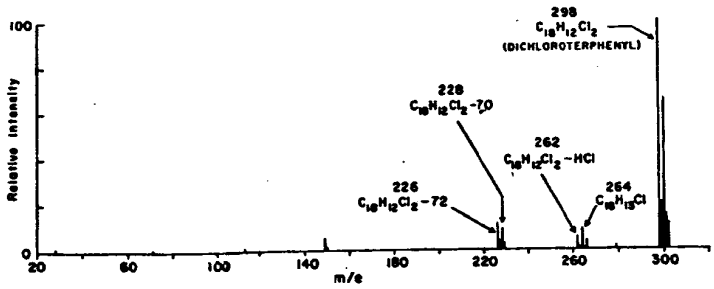

Figure 2. Mass spectrum of "TLC band B" from 3,3',4,4'-tetrachlorobiphenyl exposed to sunlight.

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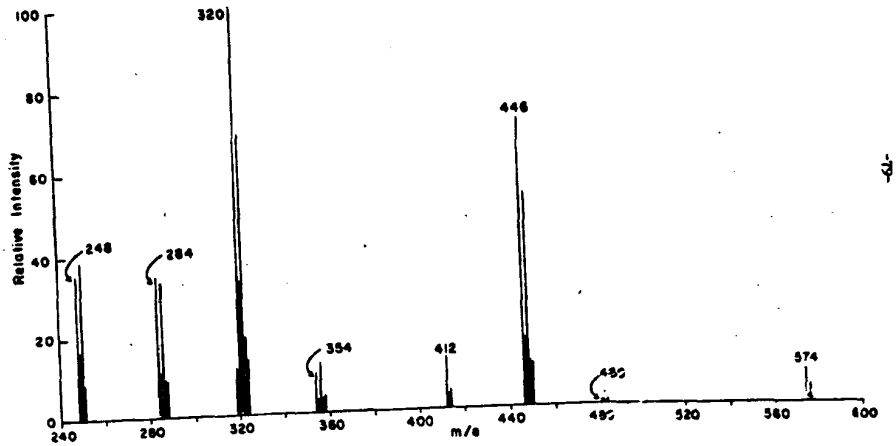

Figure 3. Mass spectrum of "TLC band B" from 2,2',4,4',5,5'-hexachlorobiphenyl exposed to sunlight.

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