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Photolysis of Hexachlorobenzene

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Photodecomposition of hexachlorobenzene exposed to sunlight as a crystalline material or on silica gel was extremely slow and no photodecomposition products were identified. This photodecomposition was sensitized by diphenylamine, but not by benzophenone. Photolysis in methanol or hexane with light of wavelengths greater than 260 or 220 nm, respectively, was rapid and the anticipated products of reductive dechlorination (pentachlorobenzene and tetrachlorobenzene) were obtained in each case. In addition, an unexpected photochemical reaction between hexachlorobenzene and methanol resulted in the formation of small amounts of pentachlorobenzyl alcohol and traces of another photoproduct that was probably a tetrachlorodi(hydroxymethyl)benzene.

Hexachlorobenzene (HCB) is an environmental contaminant that is resistant to biological degradation and demonstrates potential for accumulation in biological organisms (Metcalf et al., 1973). One of the primary sources of the compound appears to be waste streams from the manufacture of chlorinated hydrocarbons. Since HCB is relatively volatile, it may also enter the environment as a vapor in stack gases. Atmospheric transport may be responsible for the movement of HCB from contaminated areas or industrial waste dumps. Industrially, HCB has been used as a plasticizer for polyvinyl chloride.

HCB is registered as a preemergence fungicide to be used as a seed protectant for the control of certain diseases of small grains. However, its use in agriculture is minor. Although the directions for use on the label warn against the use of treated grain as human food or as animal feed, there have been instances outside the U.S.A. of contamination of food or meat when treated grain was improperly used (Schmid, 1960). In Louisiana, beef carcasses brought to slaughter in 1972 were contaminated with HCB, which could have resulted from improper disposal of industrial waste (EPA, 1973).

Decomposition by sunlight is a possible route for the environmental degradation of HCB. It is therefore important to establish the extent to which photodegradation can occur and to identify the photoproducts.

MATERIALS AND METHODS

Chemicals and Instrumental Techniques. Pentachlorobenzene was supplied by the Olin Corporation. Other compounds were synthesized by standard techniques or were obtained commercially and purified.

Low-resolution mass spectra were obtained on either a Perkin-Elmer Model GC 270 or Dupont Model 491 combination gas chromatograph–mass spectrometer using GC or direct inlet systems. Infrared spectra were recorded

in KBr disks on a Perkin-Elmer, Model 621, infrared spectrophotometer. The high-pressure liquid chromatograph (HPLC) was a DuPont Model 830, fitted with an ultraviolet photometric detector and equipped with a 1 m × 2.1 mm i.d. column packed with "Permaphase" ODS using methanol–water mixtures as the mobile phase. A Hewlett Packard Model 7600A gas chromatograph equipped with electron-capture detector and a 6 in. × 0.25 in. o.d. column packed with 3% OV-17 on Gas-Chrom Q (80–100 mesh) was used for quantitative measurements of photoproducts.

Radioactivity was measured using a Nuclear-Chicago Mark IV scintillation counter in a water-miscible counting medium [300 ml of 2-ethoxyethanol, 1500 ml of 1,4-dioxane, 18 g of 2,5-diphenyloxazole, 0.9 g of 1,4-bis[2-(5-phenyloxazolyl)]benzene, and 90 g of naphthalene].

Thin-layer chromatography was performed on silica-coated (GS 254–250 μm layer) plates with benzene as solvent.

Irradiation Experiments. (1) *Solid HCB.* A layer of crystalline HCB was placed on a glass plate under a quartz cover and exposed for 5 months to a sunlamp or to ambient laboratory illumination. Analysis was by GLC and HLPC.

(2) *On Silica Gel.* A hexane solution of HCB (0.97 μg/μl) was spotted on silica gel coated TLC plates (2 μl/spot). The plates were exposed for 4.5 h to outdoor sunlight, to a 40-W GE sunlamp (maximum output ca. 310 nm), or to laboratory illumination (fluorescent lighting). Extremely small amounts of photoproducts were observed after developing the TLC plate but the major spot was unchanged HCB.

For sensitized photolysis, 2-μl aliquots of the hexane solution of HCB were applied to silica gel coated TLC plates. Solutions of benzophenone (5 μg) or diphenylamine (5 μg) were applied to the HCB spots, and the plates were exposed to sunlight for 4.5 h, with corresponding dark controls. After development of the plates with benzene, radioautographs were obtained. A germicidal lamp was used to detect products absorbing light at 254 nm (benzenoid or aromatic compounds) which were scraped off the

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plates and extracted with ether for measurement of radioactivity. Volatility losses were measured in similar experiments.

(3) *In Methanol.* HCB (250 mg) was dispersed in methanol (250 ml). Nitrogen was bubbled through the suspension which was irradiated for 30 min with a mercury vapor lamp (Hanovia Catalog No. 679-A-36) housed in a double-walled water-cooled quartz well, as described previously (Plimmer and Hummer, 1969). A Corex filter excluded light of wavelength less than 260 nm. Analysis of products was by HLPC, GC, and TLC.

To study the course of the reaction, a similar experiment was performed using a solution of HCB (140 mg) in methanol (1 l.); samples removed at 5-min intervals were analyzed by GLC.

Two borosilicate glass Erlenmeyer flasks each containing HCB (0.5 g) dispersed in methanol (500 ml) were exposed outdoors for 12 days. The mouth of the flask was covered with a watchglass to prevent contamination. The mixture was analyzed by HPLC and mass spectrometry.

(4) *In Hexane.* HCB (1 g) in hexane (1 l.) was irradiated under nitrogen with a mercury vapor lamp for 5 min. A Vycor filter was used to exclude wavelengths less than 220 nm. Products were examined by HPLC.

RESULTS AND DISCUSSION

The direct photolysis of chlorinated aromatic compounds in solution is known to be wavelength dependent. In solvents which can function as proton donors, the predominant route of photochemical reaction is reductive dechlorination (Plimmer, 1971). The reductive dechlorination of pentachlorobenzene on photolysis in hexane gave 1,2,4,5-tetrachlorobenzene and 1,2,3,5-tetrachlorobenzene (Crosby and Hamadmad, 1971).

In these experiments, direct photolysis of hexachlorobenzene in the solid state was extremely slow. GLC examination of the solid irradiated on silica gel for 4.5 h in sunlight showed extremely small amounts of photoproducts. No photoproducts were detectable by GLC or HPLC in samples of crystalline HCB which had been exposed for 5 months to a sunlamp or laboratory illumination.

In recovery studies that were performed using ^{14}C ring-labeled HCB spotted on a silica-coated TLC plate, the plate was irradiated and developed, and the radioactivity corresponding to unchanged HCB was determined. HCB is relatively volatile, and after 4.5 h exposure to sunlight 17% of the 2 μg originally applied was lost. This loss was ascribed to volatilization, since there was no evidence of photolysis. When the effect of sensitizers was examined (Ivie and Casida, 1971), benzophenone did not significantly affect the recovery of HCB from the plate after development. Diphenylamine, however, reduced recovery to 51% of the applied material.

Tetrachlorobenzene and pentachlorobenzene were not separable from HCB in the TLC solvent system used; therefore quantitative measurements of recovered HCB also include these compounds. At least three compounds not identical with HCB were detected by autoradiography among the products of sensitized photolysis. These products have not been identified.

The observation that diphenylamine induces photolysis and that benzophenone is inactive suggests that the reaction is mechanistically similar to that suggested by Miller and Narang (1970) for the photolysis of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT). The triplet state energies (E_t) of diphenylamine (E_t = 70 kcal) and benzophenone (E_t = 69 kcal) are similar. Reaction sensitized by triplet-state energy transfer is therefore unlikely. Miller
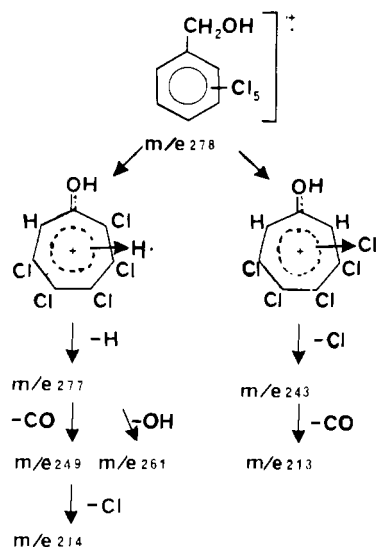

Figure 1. Rearrangement of pentachlorobenzyl alcohol to a tropylium ion.

and Narang (1970) suggest that electron transfer from the singlet state of the amine, followed by photolysis of the ground-state charge-transfer complex, affords the most attractive mechanistic possibility for reactions of this type.

Additionally there is evidence (Tosa et al., 1969) that amine-induced photolysis of halobenzenes involves the intermediacy of an excited-state change transfer complex (exciplex).

A suspension of HCB in methanol irradiated (>260 nm) for 30 min became homogeneous. The reaction products were separated by HPLC, GLC, and TLC, and identified by their infrared and mass spectra. The results were comparable to those obtained with pentachlorobenzene (Crosby and Hamadmad, 1971). The two reductive dechlorination products that were obtained were identified as pentachlorobenzene and tetrachlorobenzene. Although 1,2,3,5- and 1,2,4,5-tetrachlorobenzene were not completely resolved on GLC, retention time on GLC alone suggested that tetrachlorobenzene obtained from the photolysis was probably the 1,2,3,5 isomer.

Reductive dechlorination was not the only reaction that occurred. Two additional photolysis products were detected. Mass spectrometry of the more abundant of these products showed that the molecular ion was at m/e 278, and the distribution and intensity of spectral lines in this region indicated that five chlorine atoms were present. The molecular weight corresponded to that calculated for replacement of one Cl atom of HCB by a methoxy group. However, the fragmentation pattern was different from that of the methyl ether of pentachlorophenol that might have been expected. Examination of the spectrum of pentachlorophenyl methyl ether showed that losses of 15 (CH_3) and 43 (CH_3 + CO) mass units were major pathways of fragmentation. These were not observed in the photolysis product, but fragments at M – 1, M – 3, M – 17, M – 35, and M – 63 were observed. The base peak at M – 35 indicated loss of chlorine. Other major fragments resulted from loss of combinations of Cl, H, and CO.

This fragmentation pattern did not support an aromatic ether structure (McLafferty, 1966) and it seemed likely that the compound was a chlorinated benzyl alcohol. Since the molecular ion loses 17 (OH) and 63 (CO + Cl), fragmentation must proceed through a rearrangement process and the rearrangement of pentachlorobenzyl alcohol to a tropylium ion (Figure 1) could account for the observed fragmentation. The rearrangement of benzyl alcohol to

Table I. Percent Recovery of Products after Irradiation of HCB in Methanol 15 Days in Sunlight

Compd	% 0	% 15 days
Hexachlorobenzene	100	38
Pentachlorobenzene		3
Pentachlorobenzyl alcohol		52

a tropylium ion on electron impact is well known (Budzikiewicz et al., 1967; McLafferty, 1966).

To confirm the structural assignment, the unknown compound was acetylated. The derivative had an infrared band at 1745 cm^{-1} (ester >CO). The mass spectrum had M = 320 (5 Cl) and losses of 35, 59, 77, and 95 mass units corresponding to Cl, OCOCH$_3$, (Cl + COCH$_3$), and (Cl + CH$_3$COOH), respectively. Acetylated pentachlorobenzyl alcohol was synthesized by standard techniques and had mass and infrared spectra identical with those of the photoproduct. Their behavior on TLC and HPLC was identical. The fragmentation pattern of the other photoproduct (M = 274 (4 Cl)) resembled that of pentachlorobenzyl alcohol, precluding a methylated tetrachlorohydroxybenzene structure. After acetylation, the molecular ion was at M = 358 (4 Cl), and the fragmentation pattern indicated the addition of two acetyl groups. This evidence indicated that the photoproduct was probably a tetrachlorodi(hydroxymethyl)benzene.

Our finding that benzyl alcohols are formed in this photochemical reaction is noteworthy, since previously reported photolyses of halogenated aromatic compounds in methanol generally led to reductive dechlorination (Plimmer, 1971). Methanol is a hydrogen donor in this reaction and CH$_2$OH radicals should be formed as a result of hydrogen abstraction. With HCB this radical appears to combine with the solute to a significantly greater extent than is the case with monohalogenated aromatic systems. This suggests that the stereochemistry of the excited state–solvent complex may be important in determining the nature of the products in such photochemical reactions. Photochemical phenylation of chlorobenzenes in benzene solution suggests that there is an intimate association between solvent and reactant in the excited state (Robinson and Vernon, 1969).

In the experiment to follow the course of the reaction in methanol, only 8% of the HCB (140 mg/l.) remained after 45-min irradiation (>260 nm). The pentachlorobenzene that was formed initially decreased in quantity as tetrachlorobenzene formation increased. Pentachlorobenzyl alcohol was detected within 15 min, and reached a maximum after 30 min. At this time, the chlorinated benzyl alcohols accounted for 7.2% of the original HCB. Measurement of radioactivity showed that only 60% of the original activity was present after 30 min. The loss may be accounted for by the volatility of HCB, as well as by the volatility of the lower chlorinated benzenes. No HCB was detectable in the mixture after 85 min.

HCB in sunlight underwent similar reactions. During June and July solutions of HCB in methanol (500 mg/500 ml) contained in Erlenmeyer flasks of borosilicate glass were exposed to sunlight outdoors and the products identified were pentachlorobenzene, pentachlorobenzyl alcohol, and tetrachlorodi(hydroxymethyl)benzene. Analysis of the mixture after 15 days showed that 30% of the
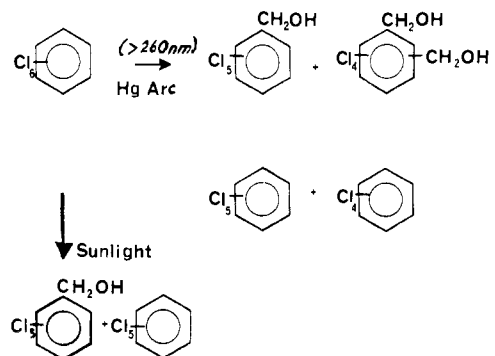

Figure 2. Photolysis of hexachlorobenzene in methanol.

HCB originally present remained (see Table I). Pentachlorobenzene represented 3% of the original material and the chlorinated benzyl alcohol fraction accounted for 52%. The photolytic pathways in methanol are summarized in Figure 2.

In hexane at wavelengths greater than 220 nm, HCB under nitrogen gave measurable amounts of pentachlorobenzene and tetrachlorobenzene within 5 min and no HCB was detectable after 15 min.

Under environmental conditions, it is to be anticipated that the photodecomposition of HCB in the solid state will be slow. In contact with organic materials the possibility of photochemical reaction is increased. Triplet sensitizers such as benzophenone do not enhance the rate of reaction, but diphenylamine sensitizes HCB photolysis on silica gel and other related amines might function in an analogous manner through a charge-transfer mechanism. Complex naturally occurring organic compounds present in rivers and streams may function as "natural" photosensitizers and may play a role in enhancing the degradation of organic pollutants by sunlight. The photolysis of HCB in the presence of "natural" photosensitizers has not been investigated, but this possibility should receive further study in view of the resistance of HCB to degradation by other routes in the environment.

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