

The Photoreduction of Pentachlorobenzenes

D. G. Crosby* and Nizar Hamadmad

Ultraviolet (2537 Å) irradiation of the fungicides pentachloronitrobenzene (PCNB), pentachlorobenzene (PCB), and pentachlorophenol (PCP) in organic solvents resulted primarily in reductive dechlorination. The nitro group in PCNB also was removed to form PCB, but corresponding nitroanilines were not detected. Reduction occurred

ortho and meta to the electron-withdrawing substituent, para to the electron-releasing group, and in para and meta positions where the substituent was H, indicative of either a free radical or hydride transfer mechanism. The compounds remained almost unchanged in sunlight, probably excluding photolysis as a major route of environmental loss.

Several pentachlorobenzenes have received wide use as pesticides. Pentachloronitrobenzene (PCNB), pentachlorophenol (PCP), hexachlorobenzene (perchlorobenzene), and pentachlorobenzene (PCB) are fungicidal, and PCP also acts as an insecticide (Martin, 1968). Application rates often are high; PCNB, for example, sometimes has been used at as much as 200 lb per acre (Thomson, 1967). The possibility that these quantities are necessary because of environmental inactivation led to an investigation of the effect of ultraviolet (uv) light on PCNB, PCP, and pentachlorobenzene.

EXPERIMENTAL

Materials. Technical pentachloronitrobenzene (Aldrich Chemical Co., Inc.) was crystallized four times from 95% ethanol to provide colorless needles, mp 143–144° C. Pentachlorophenol (Dow Chemical Co.), mp 189–190° C, was used without further purification. 2,3,4,5-, 2,3,5,6-, and 1,2,4,5-tetrachlorobenzene (Aldrich) were purified by preparative gas-liquid chromatography (glc) and were homogeneous.

Hexachlorobenzene, crystallized twice from benzene-ethanol, mp 225–226° C, was converted to pentachlorobenzene by the method of Rosenberg *et al.* (1957). The product was purified by preparative glc, mp 85–86° C (lit. 86° C; Holleman, 1920).

2,3,5,6-Tetrachlorophenol was prepared by reduction of 2,3,5,6-tetrachloronitrobenzene to the aniline by the method of Peters *et al.* (1943) and subsequent conversion of the amine to the corresponding phenol by the method of Holleman (1920). The product was purified by glc, mp 115° C (lit. 115° C; Holleman, 1921). Attempts to prepare the phenol by other routes were unsuccessful.

2,3,4,6-Tetrachloronitrobenzene was prepared from 1,3,5-trichlorobenzene (5.0 g, 0.028 mol) dissolved in 20 ml of carbon tetrachloride and treated with 0.2 g of amalgamated aluminum prepared by shaking aluminum foil with saturated aqueous mercuric chloride. The mixture then was heated to 80–90° C for 1 hr during which 0.8 g (0.011 mol) of chlorine gas was bubbled in and absorbed. After cooling, the crude

reaction mixture was treated with 12 ml of fuming nitric acid, 5 ml of concentrated nitric acid, and 2 ml of 1 M sulfuric acid, boiled under reflux for 1.5 hr with stirring, cooled, and extracted repeatedly with water. The dried organic phase (MgSO₄) was subjected to preparative glc and provided pale yellow crystals, mp 20–21° C (lit. 21–22° C; Beilstein and Kurbatow, 1878).

Glc of the chlorinated mixture before nitration permitted isolation of pure 1,2,3,5-tetrachlorobenzene, mp 51° C, and a smaller proportion of pentachlorobenzene.

Equipment. Most glc was carried out with an F&M Model 720 chromatograph employing a thermal conductivity detector, linear temperature program (5° per min), and a 2-ft × 0.25-in. stainless steel column containing 20% DC-11 silicone oil on 60/80 mesh Chromosorb W (for PCNB experiments) or 10% SE-30 gum rubber on 60/80 mesh Chromosorb P. Preparative glc was accomplished with an Aerograph Model A-70 instrument equipped with a stream splitter, flame ionization detector, and an electrostatic precipitator (Fish and Crosby, 1968); the column was 6 ft × 5/8 in. stainless steel packed with 5% DC-11 on 60/80 mesh Chromosorb P. Specific detection of chlorinated compounds was made with a Dohrman Model G-100 gas chromatograph equipped with a microcoulometric detector and a 6-ft × 0.25-in. glass column packed with 10% SE-30 on 60/80 mesh Chromosorb W.

Infrared (ir) spectra were measured (KBr) with a Perkin-Elmer Model 337 or 421 spectrophotometer; all spectra were identical with those of the authentic standards.

Irradiation. Laboratory experiments were conducted in a water-cooled reactor (Henderson and Crosby, 1967) with a low-pressure mercury arc lamp radiating at 2537 Å (Nester-Faust Manufacturing Corp.). A solution of 1 g of the compound per liter of either redistilled hexane, cyclohexane, acetone, or 95% ethanol was irradiated at 25 ± 1° C under a slight positive pressure of either dry nitrogen or air. Aliquots were withdrawn at intervals and injected directly on the gas chromatograph for analysis.

At the termination of the experiment, the irradiated solution was concentrated under reduced pressure to about 5 ml, and aliquots were subjected to glc. (PCNB precipitated from its concentrated solutions and was removed by centrifugation prior to glc.) The photoproducts were trapped in glass

Department of Environmental Toxicology, University of California, Davis, California 95616

Table I. Properties of Fractions Collected from glc

Compd irradiated	Elution temp, °C	mp, °C	Ir _{max} , cm ⁻¹	Identity
PCNB (I)	160	139-40	1445, 1325, 1111, 1053, 881, 647	IV
	182	85-86	1401, 1333, 1163, 864, 823, 685	III
	190	20-21	1550, 1348, 1163, 909, 833, 633	V
	197	65-67	1546, 1529, 1337, 925, 791, 662	VI
	208	144	1563, 1368, 1333, 942, 793, 682	I
VII	114	140	1445, 1325, 1110, 1053, 880, 647	IV
	130	45-60	1543, 1447, 1366, 1183, 813	<i>a</i>
	145	99	1425, 1337, 1176, 1111, 885, 791	VII
PCB (III)	145	51 ^b		VIII
	160	139-40	1445, 1325, 1110, 1053, 881, 647	IV
	180	85-86	1400, 1333, 1163, 865, 823, 685	III
PCP (II)	132	115	3484, 1553, 1408, 1289, 1220, 957	IX
	153	189-90	3425, 1418, 1385, 1309, 1220, 772	II

^a Mixture of trichloronitrobenzenes. ^b Identification by melting point and elution temperature only.

capillary tubes as they emerged and were purified by repeated rechromatography. Quantitative measurements were taken from standard curves representing peak area.

Irradiation by sunlight was carried out during July and August in Davis, Calif. The hexane or methanol solutions were exposed in uncovered 21 × 34 cm borosilicate glass dishes over a period of 7 days, and fresh solvent was added, as needed, to maintain volume. Alternatively, 50 ml of a 1% solution of each compound in ether was caused to evaporate evenly on the bottom of the dish to form a thin solid film. This amount (7 g/m²) corresponded roughly to the field application rate of PCNB (0.5 to 10 g/m²). In both instances, homogeneous samples were taken at 1, 3, 5, and 7 days and examined chromatographically.

Thin-layer chromatography (tlc) employed silica gel G adsorbent (phosphor) on 20-cm square glass plates. Chromatograms were developed in hexane-acetone mixtures whose composition depended on the compounds under examination.

RESULTS

Upon exposure to sunlight for 7 days, solutions of PCNB or PCP became pale yellow. However, neither glc nor tlc revealed any decomposition products, and starting materials were recovered unchanged; pentachlorobenzene solutions did not even discolor. Thin films of these compounds behaved in the same way.

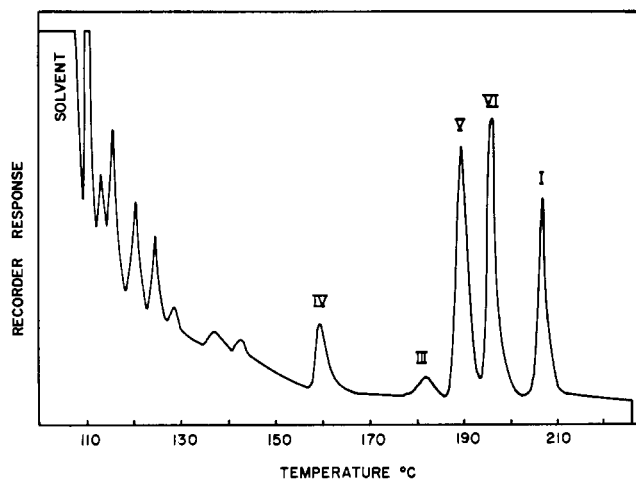


Figure 1. Typical gas chromatogram of irradiated PCNB

Irradiation of PCNB in hexane solution in the laboratory resulted in rapid discoloration, and glc (Figure 1) revealed the formation of four products in addition to unchanged starting material (Table I). The most volatile constituent of the mixture was 1,2,4,5-tetrachlorobenzene (IV); the next to elute was PCB (III), followed by 2,3,4,6-tetrachloronitrobenzene (V), 2,3,4,5-tetrachloronitrobenzene (VI), and finally PCNB itself. Unlike PCNB, V and VI were yellow and accounted in part for the color formed during irradiation.

Glc samples withdrawn at various intervals (Figure 2) revealed that III, V, and VI appeared in quantity after less than 5 min of irradiation. Their relatively constant proportions indicated steady state photolysis, although quantitative measurements showed that compounds III to VI represented 20-23% of the initial PCNB after 56 hr irradiation, while only 7% of the PCNB remained. Removal of the hexane solvent left a large proportion of dark nonvolatile tar. Increasing amounts of a number of chlorinated constituents eluting below 150°C also were observed, several of which corresponded

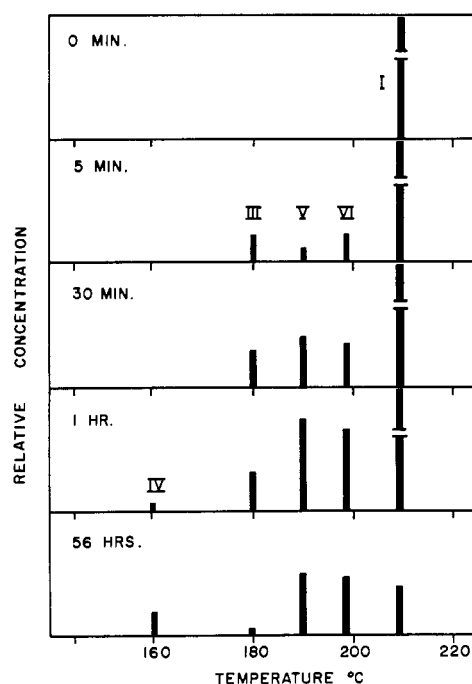


Figure 2. Time-course of PCNB photolysis (measured by glc). Bars represent peak areas

in elution temperature to di- and trichlorobenzenes, although their isolation was not attempted.

Isothermal glc of the irradiated PCNB solution with a microcoulometric (chloride) detector (180° C, N₂ flow 80 ml per min) provided peaks at 5.0 (IV), 8.5 (III), 11.0 (V), 13.0 (VI), and 18.5 min (PCNB) as well as a small distinct peak at 3.5 min attributed to VIII and a very sharp spike at 1 min associated with low boilers. Glc at 75° C resolved the spike into three peaks of equal height corresponding to 2-chlorohexane (4.0 min), 3-chlorohexane (5.0 min), and 1-chlorohexane (6.5 min).

The slow disappearance of III, proportional to the formation of IV, suggested a direct relationship between the two. However, although no 2,3,5,6-tetrachloronitrobenzene (VII) could be detected in the photolysis mixture, the possibility remained that it was converted to IV as rapidly as it formed. Irradiation of VII produced a small amount of IV, but, in fact, by far the major product was a mixture of trichloronitrobenzenes which was completely absent in the PCNB photolysis mixture. VII was not a product of PCNB photolysis.

To establish the source of IV, the authentic specimen of III also was irradiated in hexane. IV (50%) and a small amount (13%) of the isomeric 1,2,3,5-tetrachlorobenzene (VIII), but no di- or trichlorobenzenes, were formed in 3 hr of irradiation. This evidence shows clearly that IV arises exclusively from III.

Similar irradiation of PCP (II) produced only a single major decomposition product. After 32 hr, unchanged starting material (60%) and 30% of 2,3,5,6-tetrachlorophenol (IX) were identified (Sloan, 1961); a small amount (about 10%) of another phenolic substance appeared as a high-temperature shoulder on the gas chromatogram of IX and was assumed to be an isomeric tetrachlorophenol.

Figure 3 summarizes the principal photolysis products of the pentachlorobenzenes. None of these were observed when a borosilicate glass filter absorbing below 2850 Å surrounded the arc lamp, which is consistent with the results of the sunlight experiments.

DISCUSSION

Although the photoreduction of chlorinated aromatic compounds has been reported on several recent occasions (Crosby, 1966; Plimmer and Hummer, 1968), the generality of the reaction has not been recognized. The apparent unreactivity of the *p*-chlorine substituent during photolysis of PCNB indicates that the familiar ground-state reactions of *p*-nitrophenyl halides are not operative. Instead, reduction occurred in positions ortho and meta to an electron-withdrawing substituent, para to an electron-releasing group, and in intermediate para and meta positions in the case of H.

The effect of the nonhalide substituent on the position of reduction, indeed, is consistent with a free radical hydrogen abstraction from the solvent (Wolf and Kharasch, 1965), stability of the electrically neutral aromatic radical being primarily influenced by induction (Stirling, 1965). A radical mechanism also is supported by observation of very similar proportions of identical products whether irradiation was conducted in hexane, cyclohexane, acetone, or ethanol. On the other hand, expected dimeric products such as dodecanes and biphenyls were not observed, the reaction was unaffected by either the presence or absence of oxygen, and alkylated products could not be detected after photolysis in acetone, hexane, or cyclohexane.

The observed products also could be rationalized through an ionic hydride transfer mechanism, involving excited inter-

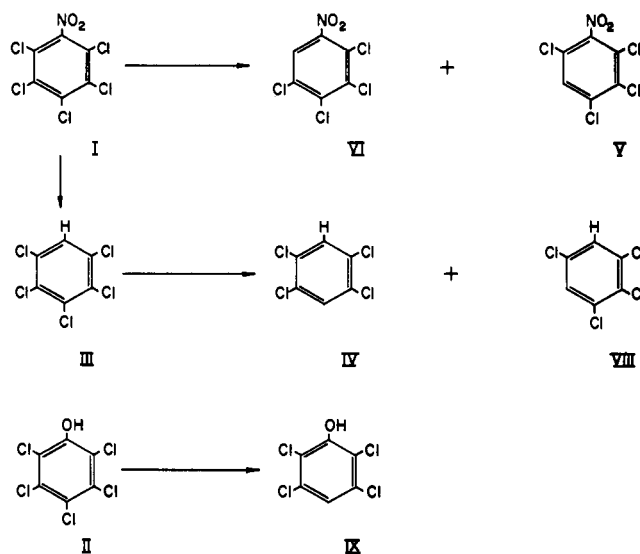
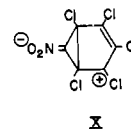


Figure 3. The photolysis of pentachlorobenzenes

mediates such as X (Zimmerman, 1963), analogous to similar photosubstitution reactions with cyanide ion (Letzinger and



McCain, 1966). The displacement of the nitro group to form IV also could be explained by either a free radical (Calvert and Pitts, 1967) or ionic mechanism (Letzinger *et al.*, 1965), although the absence of *N*-reduced products such as pentachloroaniline is contrary to the known affinity of the nitro group for hydride ions. However, present evidence favors the ionic mechanism.

Verification of chlorinated compounds with the element specific microcoulometric glc detector showed, in addition to the expected aromatic compounds, three low-boiling, chlorinated photolysis products corresponding to 1-, 2-, and 3-chlorohexane. These products account for the replaced chlorine atoms, and their appearance in equal quantity lends further support for radical formation; failure to observe other byproducts of free radical reactions could be justified on the basis of steric interference by adjacent chlorines which would restrict attack by all except the hydrogen atoms. Their presence together with the reduced (dechlorinated) aromatic compounds as the only detectable products of photolysis also demonstrates the important role which solvent may play in pesticide photolysis.

In contrast to the instability of the sodium salt of PCP (Kuwahara *et al.*, 1966) and many aromatic nitro compounds (Ellis and Wells, 1941), PCNB, PCP, and PCB underwent only very slow change in sunlight. Although definite photodecomposition of the first two was observed, both in solution and in solid films, light probably is relatively unimportant in the loss of this group of pesticides from the environment.

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