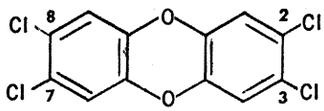
Photodecomposition of Chlorinated Dibenzo-p-Dioxins

Abstract. *The toxic herbicide impurity 2,3,7,8-tetrachlorodibenzo-p-dioxin and its homologs decomposed rapidly in alcohol solution under artificial light and natural sunlight, the rate of decomposition depending upon the degree of chlorination. However, photodecomposition was negligible in aqueous suspensions and on wet or dry soil.*

Chlorinated dibenzo-*p*-dioxins long have been recognized as by-products from the manufacture of certain chlorinated phenols (*1*). For example, 2,4,5-trichlorophenol is prepared industrially by the hydrolysis of 1,2,4,5-tetrachlorobenzene at elevated temperatures and pressures, a process which also can result in the formation of traces of heterocyclic impurities, including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (**I**).



I

This dioxin is toxic, teratogenic, and acnegenic (*1, 2*), and its presence appears to account satisfactorily for the alleged teratogenic effects of trichlorophenol derivatives such as the herbicide 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) (*3*).

Although concentrations of compound **I** in 2,4,5-T generally are low (*4*), the environmental fate of the dioxins has been a matter of concern because of extensive past use of the herbicide. Decomposition by sunlight represents one potential route of loss from the environment; previous work on the photochemical behavior of chlorinated benzenoid compounds (*5*) has shown that a ring chlorine can be replaced by hydrogen in the presence of organic solvents and by either hydrogen or the hydroxyl group in water. Accordingly, we have investigated the rates and products of the photodecomposition of homologous chlorinated dibenzo-*p*-dioxins under a variety of conditions and find that the dichloro and tetrachloro compounds indeed undergo rapid photolysis.

Light energy was provided by summer sunlight or fluorescent ultraviolet lamps known to simulate sunlight photochemically, or both (*5*). Light intensities were roughly 100 μw/cm^2 at the wavelength of maximum absorption, λ_{max}, of compound **I** (307 nm). The dioxins (*6*) initially were irradiated as homogeneous solutions in methanol or ethanol, although concentrations were limited by maximum solubilities of only a few parts per million (ppm) in these solvents. Samples were analyzed at intervals by gas chromatography with electron-capture or mass-spectrometric directors (*7*).

Typical results from the irradiation with the ultraviolet lamp of 2,7-dichloro- (**III**), 2,3,7,8-tetrachloro-, and 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (**IV**) solutions in sealed borosilicate glass containers are shown in Fig. 1. The rate of photolysis was strongly affected by the degree of chlorination. The disappearance of the tetrachloro and octachloro compounds was accompanied by the appearance of photolysis products with shorter gas chromatographic retention times; as expected, compound **I** formed 2,3,7-trichlorodibenzo-*p*-dioxin (**II**) (Fig. 2), identified by its mass spectrum, as well as even smaller amounts of a dichloro homolog. The octachloro derivative likewise produced what appeared to be a series of chlorinated dioxins of uniformly decreasing chlorine content.

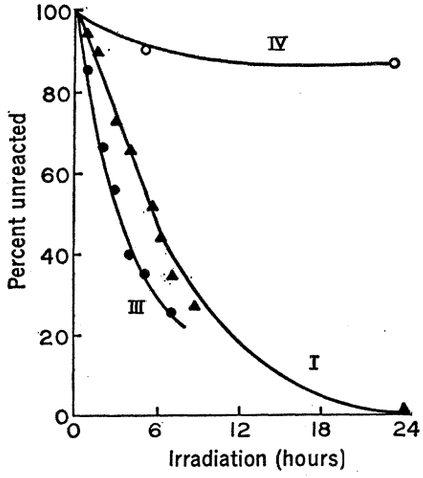


Fig. 1. Photolysis rates of chlorinated dibenzo-*p*-dioxins in methanol under ultraviolet light: 2,7-dichlorodibenzo-*p*-dioxin (**III**) (5 mg/liter); 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (**I**) (5 mg/liter); 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (**IV**) (2.2 mg/liter).

Solutions of compound **I** were exposed to natural sunlight either in open beakers or in sealed tubes; photolysis rates (Fig. 3) were similar to those found for irradiation with artificial sunlight. Continued irradiation (36 hours) eventually produced only a yellow, nonvolatile gum whose lack of any ultraviolet absorption indicated complete loss of the benzenoid chromophore. Since even the unsubstituted dibenzo-*p*-dioxin exhibited strong absorption at 290 nm, reactions other than reductive dechlorination must be involved in the photolysis of compound **I**.

In contrast to its rapid photodecomposition in organic solvents, compound **I** did not suffer appreciable loss in several other environments. For example, it was applied in 2.4 parts per million methanol solution as a spot on glass plates coated with a uniform 250-μm layer of either Norfolk sandy soil

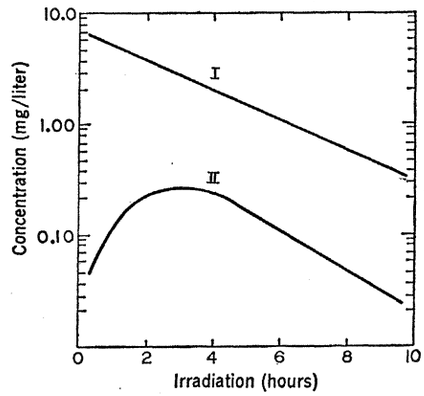


Fig. 2. Photoreduction of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (**I**) (2 mg/liter in methanol) as compared to that of the 2,3,7-trichloro homolog (**II**).

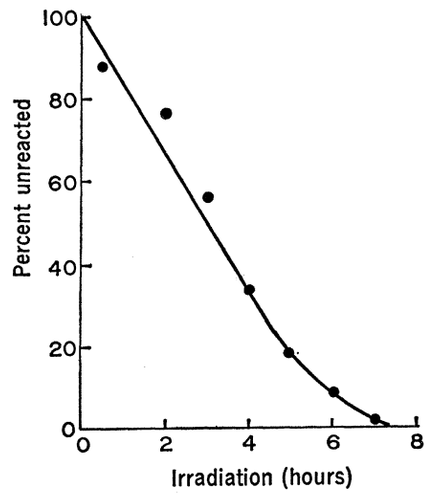


Fig. 3. Photolysis rate of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (5 mg/liter in methanol) in sunlight.

or Hagerstown silty clay loam soil. After evaporation of solvent, the plates were irradiated for 96 hours with the fluorescent ultraviolet lamp. Negligible loss due to volatilization or photolysis was observed in both instances, and compound **I** was recovered quantitatively unchanged. A second series of experiments in which the soil was kept wet with water during the irradiation gave the same result.

Irradiation of a thin dry film of compound **I** deposited by the evaporation of the methanol solution on the surface of a glass dish resulted in quantitative recovery of the dioxin after up to 14 days of irradiation. Likewise, negligible decomposition was observed upon irradiation of a suspension of compound **I** in distilled water.

These experiments, admittedly performed under idealized conditions, indicate that light of the wavelengths found in solar radiation at the earth's surface can energize the rapid destruction of compound **I** in the presence of organic hydrogen-donors. Such donors could be represented environmentally by the waxy cuticles of green leaves, surface slicks on water, or the spray oil or aromatic solvent so often incorporated into 2,4,5-T formulations (*8*). Despite the limited solubility, the organic coating of most leaves should provide adequate solvent power for the maximum of 0.27 ng/cm^2 of compound **I** which could result from a normal application of 2 pound/acre (2.25 kg/ha) of 2,4,5-T containing even 10 ppm (10 mg/kg) of the impurity.

Truly bare surfaces of soil, water, or concrete normally would offer little opportunity for the photodecomposition of compound **I**. The loss of compound **I** by evaporation is not a significant factor here, but the environmental accumulation of dioxins from repeated incidental applications presumably would occur only in the absence of biological degradation or mechanical dilution.

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3. J. E. Johnson, *Proc. Calif. Weed Conf.*, Sacramento, 18–20 January 1971, p. 43.
4. E. A. Woolson and R. F. Thomas, *Abstr. 161st Meeting, Amer. Chem. Soc.*, Los Angeles, 29 March 1971. Of 79 phenoxy herbicide samples analyzed, 53 contained less than 0.1 ppm of dioxins and 12 contained more than 10 ppm of dioxins. Current production methods hold the dioxin content below 0.5 ppm.
5. D. G. Crosby, *Residue Rev.* **25**, 1 (1969); J. R. Plimmer and B. E. Hummer, *J. Agr. Food Chem.* **17**, 83 (1969); J. R. Plimmer, *Residue Rev.* **33**, 47 (1970).
6. We are indebted to D. Firestone, Food and Drug Administration, Washington, D.C., for pure samples of the dioxins.
7. In a typical gas chromatographic analysis, we used a glass column 1.8 m by 10 mm packed with 5 percent OV-225 on 80/100-mesh Chromosorb W; column temperature, 220°C; nitrogen flow, 80 to 100 ml/min; ^{63}Ni detector at 310°C. Retention times (in minutes) were: aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-endo-exo-1,4:5,8-dimethanonaphthalene), 2.17; compound **I**, 9.40; compound **II**, 4.21; compound **III**, 2.80; and compound **IV**, 100.49. The use of 5 percent SE-30 as a liquid phase provided much shorter retention times. The mass spectrometer was a Perkin-Elmer GC-270 equipped with a surface-coated (SE-30) open tubular gas chromatographic column, 17 m by 0.51 mm. Mass spectra (mass-to-charge ratio *m/e* of the base peak, molecular ion, and characteristic fragments at 80 ev) were as follows: compound **I**, 320 ([^{35}Cl]$C_{12}H_4Cl_4O_2$), M$^+$ 320, 285 ($C_{12}H_4Cl_3O_2$), 257 ($C_{11}H_4Cl_2O$), 250 ($C_{12}H_4Cl_2O_2$), 194 ($C_{10}H_4Cl_2$); compound **II**, 286 ([^{35}Cl]$C_{12}H_5Cl_2O_2$), M$^+$ 286, 223 ($CH_{11}H_5Cl_2O$), 160 ($C_{10}H_5Cl$).
8. W. T. Thomson, *Agricultural Chemicals: Book II, Herbicides* (Simmons, Davis, Calif., 1964), p. 4; Weed Society of America, *Herbicide Handbook of the Weed Society of America* (Humphrey, Geneva, N.Y., 1967), p. 273.
9. A preliminary account of a part of this work was presented by D. G. Crosby and A. S. Wong, *Abstr. 160th Meeting, Amer. Chem. Soc.*, Chicago, 17 September 1970. Research supported in part by PHS grant ES-00054.

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Recuperation from Illness: Flavor Enhancement for Rats

Abstract. *Rats were given a distinctive fluid (milk or grape) during recuperation from an injection of a noxious drug (apomorphine). Single-bottle tests conducted after treatment indicated elevated consumption of the fluid conditionally paired with recuperation. This positive "medicinal" effect is to some degree independent of initial preference, of novelty effects, and of aversive reactions to other substances paired with the onset of illness.*

If rats drink a distinctive harmless fluid before they are made ill by x-rays or poison, they will drink less of that fluid on the next occasion. The reduction in fluid intake is proportional to the magnitude of the dose that caused the illness. This learning is remarkable because it occurs even when the illness is delayed many hours after ingestion of the flavored fluid. Furthermore, learning over such prolonged intervals may be limited to associations of food stimuli and visceral aftereffects of ingestion. Illness seems to reduce the palatability of food consumed before the onset of illness in an adaptive way for this omnivorous mammal (*1*). We are reporting here on several experiments testing the hypothesis that recuperation from illness will increase palatability. If animals drink a distinctive harmless fluid prior to recuperation from illness they should drink more of that fluid on the next occasion.

Apomorphine hydrochloride was selected as the agent because it produces an abrupt emetic illness with relatively rapid recuperation. In rats, an intraperitoneal injection (18 mg/kg) immediately causes abdominal motor spasms, huddling, and shallow breathing, and it prevents eating and drinking for about 2 hours. To determine the onset of recuperation more precisely, we tested drinking behavior in five groups of rats ($N = 4$ each) in conjunction with these injections. The animals had been habituated to drinking water only once per day during a 20-minute period in a compartment with a drinkometer. On the test day the animals were given saccharin water (1.0 g/liter) for the first time. One group was injected midway in its drinking test period; the other groups were injected 1, 2, and 3 hours before drinking. One group served as noninjected controls. All the animals injected during the drinking period stopped drinking within 2 minutes after the injection. Three of the four animals injected 1 hour before drinking did not drink, and drinking was depressed in rats injected 2 hours before the test period. The animals injected 3 hours before the test period drank as much as the noninjected controls. This emetic dose apparently produces an illness in rats that begins promptly after injection and is relatively intense for 1 hour. Recuperation appears to be under way in 2 hours and complete by 3 hours.

In experiment A we tested the effect of drinking a distinctive flavor during recuperation from a similar dose of apomorphine. Young adult female albino rats (200 to 250 g), which had