Decomposition of Aldrin by Gamma Radiation
I. In Organic Solvents

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Introduction

The extent to which chlorinated hydrocarbon insecticides have adulterated our food supply has been the subject of considerable research and discussion. The ability of various food processing techniques to decontaminate an affected comodity likewise has received considerable attention. Food preservation by gamma radiation, however, has not been studied as a means of insecticide decontamination.

The initial phase of this research was limited to studying the effect of gamma irradiation on pesticides dissolved in organic solvents using aldrin as the model.

The chemical changes which aldrin undergoes when subjected to gamma radiation have not been reported, but much information has been disseminated on the molecular changes produced by ultraviolet (UV) irradiation of aldrin.

Rosen and Sutherland (1) found that UV irradiation of aldrin in the solid state yielded unchanged aldrin, dieldrin, photodieldrin (3,4,5,6,6,7-hexachloro-12-oxahexacyclo(6.5.0.$0^{2.10}$.$0^{3.7}$.$0^{5.9}$.$0^{11.13}$.)tridecane), photoaldrin (3,4,5,6,6,7-hexachloropentacyclo (6.4.0.$0^{2.10}$.$0^{3.7}$.$0^{5.9}$.) dodec-11-ene) and polymeric material. Kawashiro et al. (2), however, did not find any dieldrin when aldrin impregnanted filter paper was UV irradiated. Henderson and Crosby (3) found only monodechlorinated aldrin (1,2,4,10,10-pentachloro-1,4,4a,5,6,8a-hexahydro-1,4-*endo*,*exo*-5,8-dimethanonaphthalene or PHDN) when hexane, cyclohexane and methanol solutions of aldrin were subjected to UV radiation.

Rosen and Carey (4) reported an interesting concentration effect with UV irradiated hexane solutions of aldrin. With an initial aldrin concentration of 7 mg/ml, they obtained only PHDN, but they obtained both PHDN and photoaldrin when the initial concentration was 1 mg/ml. Photoaldrin and PHDN were isolated from ethyl acetate solutions of aldrin UV irradiated under a carbon dioxide blanket for seven days (5).

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Bulla and Edgerley (6) studied the degradation of aldrin, dieldrin and endrin by UV light as a process to be used in water pollution abatement. Aldrin was degraded the most and dieldrin the least. The irradiated aldrin solution (the only one tested) was less toxic to bluegill fingerlings than was the nonirradiated control.

Experimental

Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1, 4-*endo*,*exo*-5,8-dimethanonaphthalene) of stated 99+% purity was obtained through the courtesy of the Shell Chemical Co., New York, New York.

High purity n-hexane, 99% pure cyclohexane (both from Phillips Petroleum Co., Buctlesville, Okla.) and 99.5% USP grade acetone (Lynn Chemical Co., Indianapolis, Indiana) were all glass distilled prior to use.

Irradiations were accomplished with a U.S. Nuclear Model GR-12 irradiator (U.S. Nuclear Corp., Burbank, Calif.) containing 7500 curie ^{60}Co source.

Methods. The changes caused by gamma radiation were studied by varying concentrations of aldrin, the total dose of gamma radiation absorbed by the aldrin solutions, the temperature at which the irradiation was accomplished, and various solvents used to dissolve the aldrin.

Stock solutions of aldrin dissolved in hexane, acetone and cyclohexane were prepared to concentrations of 1000 ppm.

Ten ml aliquots of the solution under study were added to screw-capped culture tubes (16x125mm), the caps of which were lined with aluminum foil. In some cases larger amounts of the solutions were irradiated in 200 ml bottles with teflon lined screw caps. All irradiations were performed in an atmosphere of air and were at $0^{\circ}C \pm 0.5^{\circ}C$ except when the effect of temperature was under study. The tubes were suspended up to their caps in the jacketed cold chamber accessory of the irradiator through which ethylene glycol circulated as the refrigerant. The tubes in the inner chamber of the accessory, were surrounded with methyl alcohol which served as a heat transfer agent between the tubes and the wall. The temperature of the ethylene glycol was maintained by a refrigerant bath external to the irradiator.

Samples were irradiated at $-196^{\circ}C$ by placing the tubes in a 250 ml Dewar flask containing liquid nitrogen which was replenished at approximately three hour intervals during the irradiation. Samples were irradiated without temperature control by suspending the sample tubes into the cold chamber without circulating the refrigerant.

The absorbed dose rate was determined with a Fricke (ferrous sulfate) dosimeter, as reported by Spinks and Woods (7), with the following modification; Sterile water for injections (U.S.P., Abbott Laboratories, Chicago, Illinois) was used to prepare the chemical dosimeter. Irradiation time was three minutes, after which the absorbance was measured on a Beckman DU spectrophotometer at 304.5 mu. The blank was an unirradiated dosimeter solution. The absorbed dose rate was 3.4×10^5 rads per hour for 10 ml sample in the 20 ml bottles. (The bottles also were placed in the cold chamber and surrounded by methyl alcohol.)

Samples irradiated at -196°C were stored in liquid nitrogen until analyzed but other samples were stored at -20°C.

Samples were irradiated in duplicate and solvent blanks were irradiated throughout the course of these experiments.

Analysis of Samples. The irradiated aldrin-hexane solutions did not require clean-up. An aliquot of the sample was diluted to one ppm assuming no degradation of the aldrin due to irradiation. Aliquots of the acetone and cyclohexane solutions of aldrin, on the other hand, were evaporated just to dryness under a very gentle stream of purified nitrogen in a water bath at 40°C. They were diluted with hexane to a concentration of one ppm of aldrin again assuming there was no degradation of the aldrin due to irradiation. The diluted samples were subjected to gas chromatographic analysis. The control samples were handled in an identical manner.

A preparatory scale sample of an aldrin-hexane solution was prepared by irradiating (at 6.0 Mrad) one liter of a 2000 ppm solution without any temperature control and then concentrating it by rotary evaporation until a dark viscous fluid remained in the flask (about 5 ml). Aliquots of this liquid were injected into a gas chromatograph and some of the compounds represented by the peaks were collected for infrared analysis.

Three hundred milliliters of the aldrin-hexane stock solution were irradiated at 6.0 Mrad without any temperature control and then concentration to about 6 ml using a Kuderna-Danish concentrator (Konte Glass Co., Vineland, N.J.). This solution was used for mass spectrometric analysis.

For gas chromatographic analytical determinations Aerograph Pestilyzer Model 680 gas chromatograph (Varian-Aerograph, Walnut Creek, California) containing a 250 millicurie tritium foil electron capture detector was used. Two 5' x 1/8" glass columns were used. The first contained 5% DC 200 silicone oil on Gas Chrom Q 100/200 mesh at an oven temperature of 200°C and a nitrogen flow rate of 58 ml/minute. The injector port and the detector were at 200°C. The second column was 3% SE 30 silicone gum on Gas Chrom Q 80/100 mesh at an oven temperature of 185°C and a nitrogen carrier gas flow rate of 66 ml/minute. The injector port and the detector

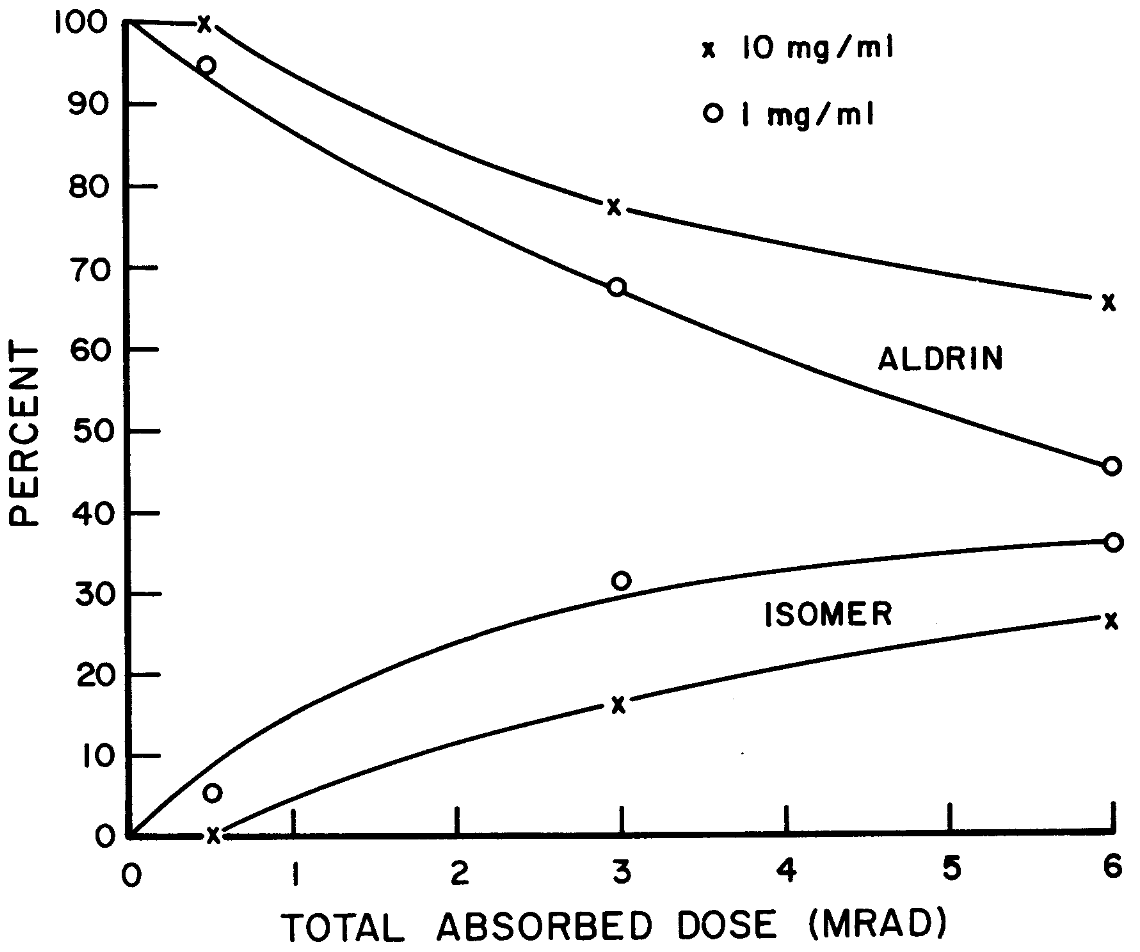

Figure 1. Percent of Undegraded Aldrin and Main Radiation Isomer in Aldrin-Hexane Solution After Gamma Irradiation at Various Dosages.

were at 185°C. Duplicate samples were injected into the DC 200 column, but on the SE 30 column single samples were analyzed. The chromatographs obtained on these two columns were similar. The chromatographs from the DC 200 column were used for quantitation by the peak height method (8).

The concentrated preparatory sample was injected, 5 ul at a time, into an Aerograph A-600B gas chromatograph equipped with a flame ionization detector. A 6' x ¼" stainless steel column containing 3% SE 30 on Gas Chrom Q 80/100 mesh was used. At the end of the column, just in front of the detector, was a 10:1 micro-sample splitter-collector (Varian-Aerograph) from which various compounds were collected into melting point cappillary tubes. The oven temperature was manually programmed from about 135°C to 180°C. The injector port was at 200°C and the detector temperature varied with the oven temperature.

The compounds collected from the preparative gas chromatograph for infrared analysis were transferred to KBr wedges (Wicksticks) (9). Five millimeter micropellets were pressed using the Carle Pellet Die Ring Holder Kit. (Carle Instruments, Inc., Fullerton, California.)

A Beckman IR 8 spectrophotometer equipped with a mirror beam condenser (T attachment, Beckman Instruments, Inc., Fullerton, California) was used to record the spectra of the samples.

For mass spectrometric measurements portions of the concentrated solution from the irradiation of 300 ml of the aldrin-hexane solution were injected into an LKB Gas Chromatograph-Mass Spectrometer Type 9000 (LKB Instruments, Inc., Rockville, Maryland). The gas chromatographic unit contained an 8' x ¼" glass column packed with 3% SE 30 on a silanized support. Injector and detector temperatures were maintained at 250°C and the column was programmed from 150°C to 300°C at 5° C/minute. The electron current for the first scan was 70 eV and for the second scan was 20 eV. The scan width was 480 mass units beginning with zero.

Results and Discussion

Aldrin, dissolved in hexane in initial concentrations of 1 mg/ml and 10 mg/ml, was irradiated at three different dosages: 0.5 Mrad, 3.0 Mrad and 6.0 Mrad. The results are summarized in Table 1. As expected, as the total absorbed dose increased, the decomposition of aldrin increased. The percent of undegraded aldrin remaining in each sample after irradiation is shown graphically in Figure 1.

As the percent of aldrin remaining in the sample decreased, the amounts of the products formed increased. The major radiation product (as indicated by the peak height column of Table 1) has a retention time relative to aldrin of 0.72. The effect of absorbed dose and aldrin concentration on the percent increase of this isomer in each sample also appears in Figure 1.

TABLE 1

Summary of Gas Chromatographic Data[a] of Aldrin Irradiated in Hexane at Two Concentrations and Three Dosages.

Total Absorbed Dose (Mrad)	Initial Concentration (ppm)	Peak No.	Retention Time Relative to Aldrin[b]	Peak Height (cm)[c]
0.5	1,000	1	0.72	0.45
		2	1.00	7.95
	10,000	1	1.00	8.18
3.0	1,000	1	0.72	3.17
		2	1.00	6.90
		3	1.21	0.20
		4	1.79	very small
	10,000	1	0.72	1.60
		2	1.00	7.77
		3	1.20	0.70
		4	1.79	very small
6.0	1,000	1	0.54	0.43
		2	0.72	5.20
		3	0.90	0.85
		4	1.00	6.60
		5	1.21	1.25
		6	1.80	0.35
	10,000	1	0.72	2.95
		2	1.00	7.30
		3	1.20	1.00
		4	1.79	very small

[a] Gas chromatograph column: 5/ DC 200 on Gas Chrom Q 100/120 mesh

[b] Retention time of aldrin = 1.65 min.

[c] Average of two replicates

TABLE 2

Retention Values Relative to Aldrin[a] of Peaks in Aldrin-Hexane Solution Irradiated at Different Temperatures.

	Peak Number									
Temperature	1	2	3	4	5	6	7	8	9	10
-196°	-	0.71	0.80	-	1.00	1.19	-	-	-	-
0°	0.52	0.71	-	0.86	1.00	1.19	1.81	-	2.10	-
varied[b]	0.52	0.71	-	0.86	1.00	1.19	-	1.93	-	5.50

[a] Retention time of aldrin = 1.65 min.

[b] Starting temperature 27°C. Final temperature 45°C (attained in 500 minutes).

The second most intense new peak formed by irradiation of aldrin dissolved in hexane was one with a retention time relative to aldrin of 1.20 (Table 1). In contrast to the 0.72 peak, the percent of the 1.20 compound was greater in the 10 mg/ml sample than it was in the 1 mg/ml sample.

Effect of Temperature. The temperature at which irradiation was performed played a significant role. A 1 mg/ml hexane solution of aldrin was irradiated to a total absorbed dose of 6.0 Mrad at -196°C, 0°C and at an uncontrolled temperature. (The temperature increased from 27° to 45°C). The samples were stored as indicated previously. The results of the gas chromatographic analyses using the DC 200 column are shown in Table 2. Peaks numbered 1, 3, 4, 7, 8, 9 and 10 were minor, while the compound represented by peak 2 again was the major radiation isomer.

An analysis of variance and Duncan's New Multiple Range Test (10) were used to test the significance of the percentages of similar compounds appearing at each irradiation temperature. The amounts of the common compounds in each sample are shown in Table 3. The amount of the 0.71-0.72 compound increased significantly with temperature, while that of the 1.19-1.20 compound decreased as temperature increased. The amount of undegraded aldrin increased significantly at -196°C, but no meaningful difference was found between the amount left at 0°C and that remaining in the sample where temperature was not controlled.

TABLE 3

Effect of Temperature on the Peak Height of Similar Peaks in Each Sample of Irradiated Aldrin-Hexane Solution as Indicated by Percentage.

	Peak (Relative Retention Value)		
Temperature	0.71	1.00	1.19
	%	%	%
-196°C	14.85	62.50	13.68
0°C	36.25	41.40[c]	9.84
varied[a][b]	39.35	41.50[c]	5.26

[a] Start 27°C. Final 45°C (attained in 500 minutes).

[b] Stored at -20°C.

[c] Not significant at the 5% level of significance.

Effect of Solvent. Since free radicals from the solvent can be responsible for the decomposition of the solute, (11) the products formed in irradiated aldrin solutions could possibly vary with different solvents.

In addition to aldrin-hexane solutions, aldrin-acetone and aldrin-cyclohexane solutions at an initial concentration of 1 mg/ml were irradiated to a dosage of 6.0 Mrad at 0°C.

Fifteen peaks were recorded in the gas chromatogram of the irradiated aldrin-acetone solution. The major peak has a retention time of about 7 minutes while the final peak appeared in about 19 minutes. Aldrin had a retention time of about 1.3 minutes and was present in small quantity.

The irradiated aldrin-cyclohexane chromatogram revealed 14 peaks, the last one emerging in about 15 minutes. In spite of the number of peaks, the unaltered aldrin was the largest peak in the chromatogram.

In contrast to the number and long retention times of the peaks of the previous two aldrin solutions, the chromatogram of the irradiated aldrin-hexane solution revealed only 7 peaks, the last having a retention time of slightly less than three minutes. Aldrin was approximately 65% degraded when irradiated in a hexane solution at 0°C using total absorbed dose of 6.0 Mrad.

All irradiated solutions had a sharp, pungent odor after the treatment, and the hexane solution became yellow upon concentration. The odor of chlorine gas was evident when larger volumes of the aldrin-hexane solution were irradiated.

The mass spectrum of the 0.71-0.72 peak indicated the isomer was a pentachloro derivative of aldrin. The parent peak of the spectrum was at m/e 328 and no peaks beyond m/e 332 were found in either of the 70 eV spectra. The remainder of the spectrum was consistent with the idea of mono dechlorination of the parent compound. In addition, the peak at mass 101 was very small, but it is one of the 5 major peaks in the aldrin spectrum (12). The decrease in the peak at mass 101 may be due to a rearrangement or a chlorine loss from the chlorinated bridge (13).

Since one of the UV degradation products of an aldrin-hexane solution was the monodechlorinated isomer, PHDN (3, 4) and since the gas chromatographic retention time of PHDN relative to aldrin was 0.8 (3), it was possible that the primary gamma radiation induced isomer in this system was also PHDN. This did not prove to be the case, however, since the IR spectrum of PHDN (14) and that of the 0.71-0.72 isomer were not identical. The PHDN spectrum exhibited strong bands at wavelengths of 9.40μ, 9.86μ, 10.80μ, 11.70μ, 12.47μ, 13.38μ, which were absent from the 0.71-0.72 spectrum. On the other hand, the strong bands at 3.38μ, 11.42μ, 12.38μ, 12.53μ, in the 0.71-0.72 spectrum were absent from the PHDN spectrum. In addition, the strong 8.59μ bank in the 0.71-0.72 spectrum was weak in the PHDN spectrum, and several bands of the medium intensity were found in each spectrum which were absent from the other spectrum.

The IR spectrum of the 0.71-0.72 isomer exhibited an olefin absorption at 3.29μ, but the cis-olefin absorption may have shifted from 13.90μ in aldrin to about 14.20μ in the gamma radiation induced isomer. A peak at 14.20μ also occurred in the PHDN spectrum. Although a peak at 6.25μ was not as strong in the 0.71-0.72 isomer as it was in aldrin and PHDN, it was still indicative of the presence of the chlorinated olefin group. A peak at about 6.8μ was evidence for the presence of the methylene bridge in the non-chlorinated portion of the molecule. The identification and toxicity of this isomer remain to be determined.

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