Decomposition of Aldrin by Gamma Radiation
II. In Lipid Solutions

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Introduction

Carp et al. (1) studied the effect of gamma irradiation on aldrin dissolved in organic solvents. They found that the extent of aldrin degradation and the number of isomers produced by the radiation varied with the absorbed dose of gamma radiation, the concentration of the aldrin, the solvent used to dissolve the pesticide and the temperature at which irradiation occurred.

This work was extended by dissolving the aldrin in corn oil and lard and varying the conditions used in packing, irradiating and storing the samples.

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. The Phillips Petroleum Co., Bartlesville, Oklahoma was the source of the 99% hexane which was glass distilled in our laboratory prior to use.

All irradiations were accomplished with a U.S. Nuclear Model GR-12 irradiator (U.S. Nuclear Corp. Burbank, California) containing a 7500 curie ^{60}Co source. Corn oil and pure lard were purchased from a local supermarket.

A stock solution of aldrin dissolved in corn oil was prepared by adding 1.0 g aldrin to 999.0 g corn oil. The lard stock solution was prepared by dissolving 0.5 g aldrin in 499.5 g of molten lard at 55°C. (The lard was liquified in a 55°C water bath and was always in the liquid state when handled.) Aliquots of approximately 10 g each were added to screw-capped culture tubes which then were irradiated.

Aldrin was irradiated under the following conditions. It was dissolved in two lipids - corn oil and lard; it was irradiated

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2/Journal Paper #4197 of the Purdue Agricultural Experiment Station

Bulletin of Environmental Contamination & Toxicology, Vol. 7, No. 6, 1972, © by Springer-Verlag New York Inc.

without any temperature control and at -196°C; half of the lard and corn oil samples were packed in air while the other half were nitrogen-packed; after irradiation the samples were stored at room temperature in the dark and at -20°C in the dark. A 2^4 factorial experiment was designed for the above conditions.

The procedure for deaeration and nitrogen packing of the samples was suggested by Swallow (2). A plastic glove box with an airlock attachment (Manostat Plastic Glove Box No. 41-906-12, Manostat Corp., New York, N. Y.) was deaerated to 2% oxygen and 98% nitrogen by alternately evacuating with an external vacuum pump and then flushing with high purity nitrogen gas. The culture tubes containing the lipid samples to be nitrogen packed were capped with serum bottle stoppers and glass tubing was inserted through each stopper into the head space above the sample. Inside the glove box, the corn oil samples were solidified rapidly in liquid nitrogen and then attached to the vacuum line via the glass tubing. After evacuating the gas from the solid samples, the tubes were reliquified in a 50-60°C water bath. When foaming ceased, the cycle was repeated by resolidifying, evacuating and reliquifying under vacuum. The serum caps were removed, and a stream of nitrogen gas was directed into each tube which then was capped with a silicone rubber lined screw cap. The lard samples were processed in an identical manner except that they were melted in the 50-60°C water bath prior to the initial solidification. Due to the constant evaporation of liquid nitrogen from the Dewar flasks inside the glove box, a positive pressure of nitrogen was maintained continually.

Samples were irradiated in duplicate, and blanks (lipid only) were irradiated with each sample. Control samples were maintained and stored under the same temperature conditions as their irradiated counterparts, but they were not irradiated. Therefore, each sample had four components, an original sample, the duplicate, the control and the blank. The original sample, duplicate and blank always were irradiated as a unit, and no sample components were split. The aldrin concentration was constant at 1 mg per ml and the total absorbed dose was always 6.0 Mrad.

All culture tubes were irradiated in beakers. The samples irradiated without any temperature control (B_1 samples) were at room temperature at the start of the treatment but attained a temperature of 39° - 40°C within 2.5 hours and maintained that temperature for the remainder of the irradiation. The control B_1 samples were stored in a 40°C incubator for a length of time comparable to the irradiation time. Liquid nitrogen was added to the beaker containing the -196°C (B_2) samples every 30 minutes throughout the irradiation. Control B_2 samples also were kept in liquid nitrogen throughout the irradiation period.

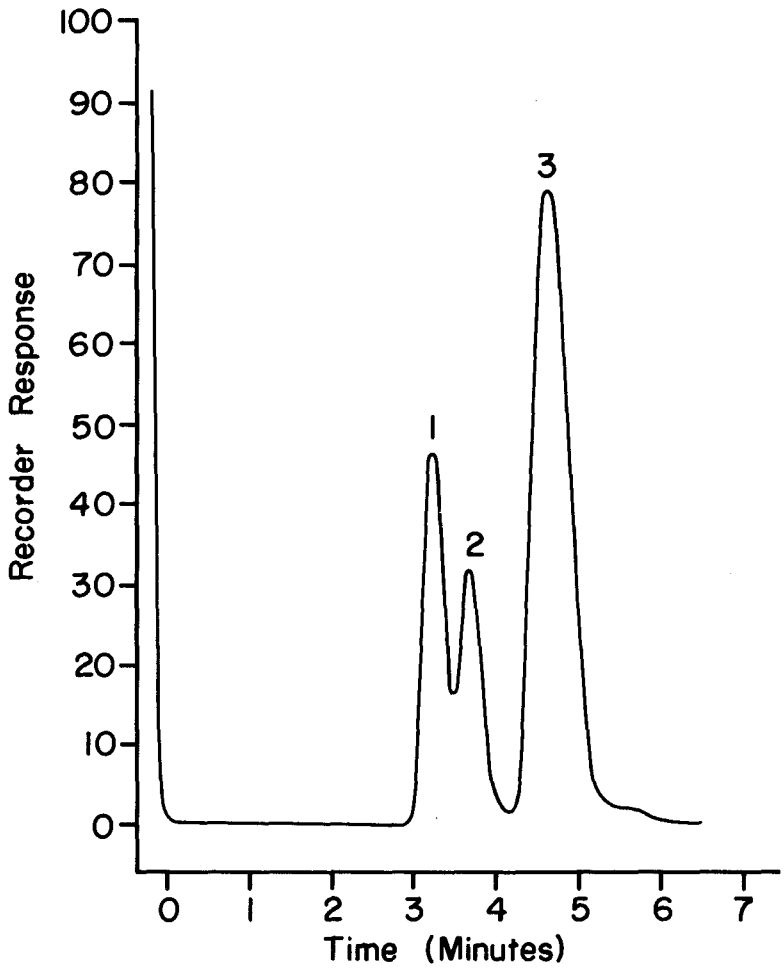

Figure 1. Typical Gas Chromatograms of Gamma Irradiated Aldrin-Lipid Solutions Irradiated at -196°C.

A Fricke dosimeter was used for the absorbed dose determination. Air was used as the heat transfer medium in the beaker. The absorbed dose rate was 0.381 Mrad. per hour.

The lipid samples were extracted and cleaned-up using the procedure of Langlois et al. (3). One-half gram of lipid sample was weighed accurately onto about 25 g of the partially deactivated florisil. This was ground in a mortar with a pestle until free flowing and then added to prewashed florisil in the column. The aldrin was eluted from the column with 400 ml of the eluant. The eluant mixture was evaporated just to dryness in a 55°C water bath and hexane was added immediately to the beaker. The aldrin was transferred quantitatively with hexane from the beaker to a 100 ml volumetric flask and made to volume. The sample was diluted another 10-fold, and this final dilution was used for gas chromatographic analysis. Recovery exceeded 95%.

The hexane solutions from the lipid samples were analyzed on an Aerograph A-600 gas chromatograph (Varian-Aerograph, Walnut Creek, California) equipped with a 250 mCi tritium foil electron capture detector. Two 5' x 1/8" glass columns were used. One column was 5% DC 200 silicone oil on Gas Chrom Q 100/200 mesh at an oven temperature of 195°C and a nitrogen flow rate of 71 ml/minute. 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 flow rate of 66 ml/minute. In both cases the injector temperature was at 210°C. The chromatograms obtained on both columns were similar.

Results and Discussion

The chromatograms of the samples irradiated without any temperature control generally showed four peaks, while those irradiated at -196°C showed only three (Figure 1). The three major peaks in both cases had identical relative retention times (relative to aldrin). Peak 1 was about 0.70, peak 2 about 0.80 and peak 3 was undegraded aldrin. The fourth peak mentioned above was very minor and appeared between 2 to 3 minutes.

The cleaned-up control samples gave only an aldrin peak, while the cleaned-up blank samples did not produce any peaks.

Quantitation of the three identical peaks was achieved by triangulation as suggested by Gual (4).

The percent of the three similar peaks in each lipid sample is presented in Table 1. An examination of this table reveals that irradiation temperature was most important in determining the amount of degradation products represented by Peaks 1 and 2. Peak 1 was approximately 11% larger in the samples irradiated without temperature control than it was in samples irradiated at -196°C. In contrast, peak 2 was almost 7% smaller in the warmer samples than it was in those irradiated in liquid nitrogen.

These results are similar to those obtained with irradiated aldrin-hexane solutions (1). The other treatments individually has essentially no effect on the size of the two peaks.

TABLE 1

Percent of Similar Peaks in Each Sample of Gamma Irradiated Aldrin-Lipid Solutions.

Corn Oil (A_1)				Lard (A_2)			
Treatment	Peak 1	2	3	Treatment	Peak 1	2	3
	%	%	%		%	%	%
$B_1C_1D_1$[ab]	29.32	7.59	63.10	$B_1C_1D_1$	29.10	6.84	64.06
$B_2C_1D_1$	19.02	13.55	67.43	$B_2C_1D_1$	18.89	10.91	70.21
$B_1C_2D_1$	30.38	7.30	61.88	$B_1C_2D_1$	31.77	5.99	62.24
$B_1C_1D_2$	31.18	7.76	61.07	$B_1C_1D_2$	31.23	6.37	62.40
$B_2C_2D_1$	20.56	17.11	62.53	$B_2C_2D_1$	20.58	15.76	63.67
$B_2C_1D_2$	19.67	16.01	64.32	$B_2C_1D_2$	18.29	14.69	66.82
$B_1C_2D_2$	30.36	8.95	60.69	$B_1C_2D_2$	29.82	9.51	60.67
$B_2C_2D_2$	19.52	14.91	65.57	$B_2C_2D_2$	19.26	13.35	67.40

[a]Percentages listed are the means of 4 replicates, 2 from the sample and 2 from the duplicate.

[b]B_1 = irradiated without temperature control; B_2 = irradiated at -196°C; C_1 = air pack; C_2 = N_2 pack; D_1 = stored at room temperature; D_2 = stored at -20°.

The value for peak 3, the undegraded aldrin, actually is the sum of peaks 1 and 2 subtracted from 100%. Consequently, the results of each treatment on peak 3 will be the net effect of each treatment on the other two peaks.

To test the significance of the main effects and interactions, an analysis of variance was performed on each of the three similar peaks by the method of orthogonal contrasts (5). The test of significance was at the 5% level of probability. A summary of this analysis is shown in Table 2. While several statistically significant treatments and interactions are indicated, the results emphasize the large temperature effect in contrast to the other treatments.

The CD interactions of peaks 1 and 2 are significant only because of a change of direction rather than a change in magnitude (5). All four main effects appear to significantly alter the amount of peak 2 in each of the samples, but only the temperature effect has any practical significance. The observation

TABLE 2

Analysis of Variance of Similar Peaks of Irradiated Aldrin-Lipid Solutions.

Treatment[a]	Peak 1 S.S.	df	M.S.	Peak 2 S.S.	df	M.S.	Peak 3 S.S.	df	M.S.
A	0.289	1		11.448	1	16.308**	14.797	1	5.416*
B	964.044	1	553.826**	394.524	1	562.000**	126.723	1	46.385**
AB	0.495	1		1.796	1	2.558ns	3.920	1	
C	4.515	1	2.593ns	10.035	1	14.295**	27.195	1	9.954**
AC	0.423	1		0.622	1		2.279	1	
BC	0.551	1		0.819	1		2.498	1	
D	0.066	1		5.611	1	7.993*	4.759	1	
AD	0.938	1		0.800	1		0.021	1	
BD	1.882	1		1.155	1		5.662	1	2.072ns
CD	9.746	1	5.599*	3.892	1	5.544*	25.205	1	9.226
ABC	0.060	1		0.038	1		2.940	1	
ABD	0.010	1		0.001	1		0.023	1	
ACD	0.080	1		0.078	1		0.006	1	
BCD	1.980	1		34.114	1	48.595**	19.035	1	6.967*
ABCD	1.304	1		2.258	1	3.217ns	0.370	1	
	986.383	15		467.191	15		235.443	15	
Error	26.111	15	1.741	Error 10.534	15	0.702	Error 40.973	15	2.732
Total	1012.494	30		Total 477.725	30		276.416	30	

[a]Treatment: A = lipid;
B = irradiation temperature
C = irradiation atmosphere
D = storage temperature

that both treatments A and B were highly significant statistically but that no significant AB interaction was evident emphasized the independent nature of the two treatments regarding peak 2. The samples irradiated in air at -196°C and stored at room temperature had about 4% less of peak 2 than those irradiated in nitrogen at -196°C and stored at room temperature. Because of this decrease, there is a highly significant BCD interaction.

At an initial concentration of 1 mg/ml, aldrin was degraded approximately 20% in the lipid samples which were gamma irradiated to an absorbed dose of 6.0 Mrad.

The only treatment which produced any major alteration of the amounts of the isomers formed was the temperature at which irradiation was accomplished. Approximately 4% more aldrin was evident when the pesticide was gamma irradiated at -196°C than when it was irradiated at temperatures varying from room temperature to about 40°C. The gaseous atmosphere surrounding the samples significantly affected peak 2 when the samples were irradiated at -196°C and stored at room temperature in the dark.

The chemical identity of the major isomers as well as their toxicity should be determined to more completely evaluate the efficiency of gamma irradiation as a decontaminant for aldrin in these systems.

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