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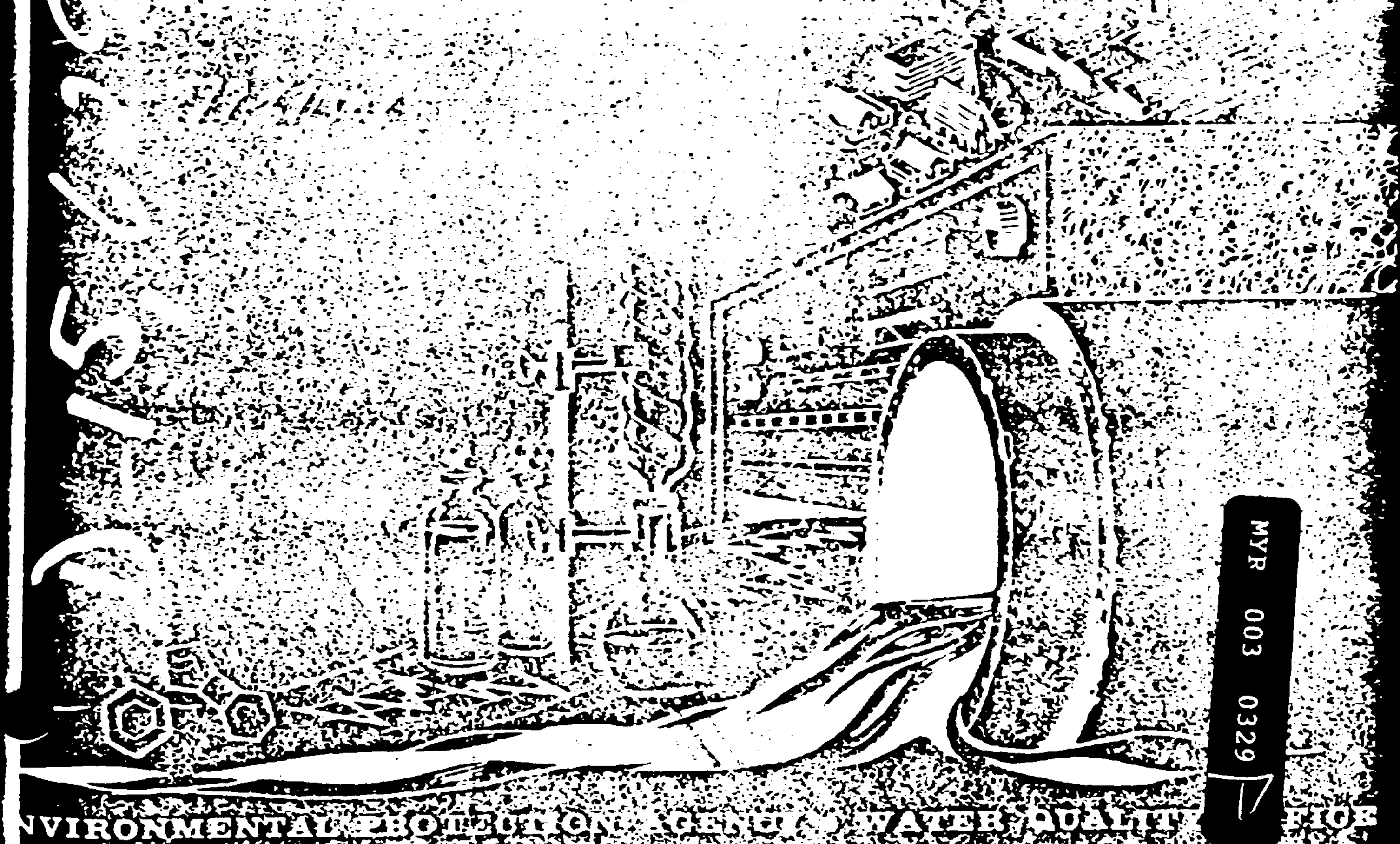
Investigation of Means for Controlled Self-Destruction of Pesticides



NVIRONMENTAL PROTECTION AGENCY • WATER QUALITY OFFICE

INVESTIGATION OF MEANS FOR CONTROLLED SELF-DESTRUCTION OF PESTICIDES

by

AEROJET-GENERAL CORPORATION
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for the

WATER QUALITY OFFICE
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7 *Abstract*

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Chemical methods for degrading DDT were screened and reduction was selected as he most promising technique. Destruction of DDT, without forming DDE as a product, as demonstrated by mildly acidic reduction with zinc powder. The principal product is is(p-chlorophenyl)ethane, DDT with all three aliphatic chlorines removed; a material tated to be "void of the neurotoxic effects of DDT." Catalysis of the reaction resulted n complete destruction of DDT in 1 hr at 25°C and conversion to bis(chlorophenyl)ethane n 4-8 hrs. Catalyzed aluminum or iron reduction of DDT produced tetra(p-chlorophenyl)-etrachlorobutane, reportedly lipoid insoluble. Reductive degradation of dieldrin, endrin, ldrin, chlordane, heptachlor, toxaphene, and selected polychlorinated biphenyls was lso shown.

A 90% destruction of DDT in laboratory soil was shown in 4 days by this technique. Degradation of DDT in water was demonstrated also, a 421 mg/l suspension being reduced to 1 ppm after 1 hr reaction at 75°C.

Reaction delay can be achieved with wax or silyl coatings which are slowly dissolved r eroded. Coatings were produced which stopped zinc-acid reaction.

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ABSTRACT

Laboratory studies demonstrated the feasibility of controlled destruction of chlorinated pesticides such as DDT.* The concept comprised (1) means to degrade DDT to a harmless form, and (2) methods to delay the reaction for given pest-control action.

Chemical methods for degrading DDT were screened and reduction was selected as the most promising technique. Destruction of DDT, without forming DDE as a product, was demonstrated in laboratory studies by mildly acidic reduction with zinc powder. The principal product is bis(p-chlorophenyl) ethane, DDT with all three aliphatic chlorines removed; a material stated to be "void of the neurotoxic effects of DDT." Catalysis of the reaction resulted in complete destruction of DDT in 1 hr at 25°C and conversion to bis(chlorophenyl) ethane in 4-8 hrs. Catalyzed aluminum or iron reduction of DDT produced tetra(p-chlorophenyl)tetrachlorobutane, reportedly lipoid insoluble.

A 90% destruction of DDT in soil in 4 days was demonstrated in a laboratory test with spray-applied integral, catalyzed zinc-DDT particles (5-micron).

Reaction delay can be achieved with wax or silicone coatings on the reductant which are slowly dissolved or eroded, or possibly slow air oxidation of sulfur. Coatings were produced which stopped zinc-acid reaction. A test of combined reductant - delayed action technique was made using silanized, catalyzed zinc (5 microns)-DDT particles sprayed onto soil. Although faulty coating prevented the desired delay, 95% decomposition of DDT was obtained.

Effective reductive degradation of the chlorinated pesticides dieldrin, endrin, aldrin, chlordane, toxaphene, Kelthane, methoxychlor, Perthane and lindane, and selected polychlorinated biphenyls was shown.

Degradation of DDT in water was demonstrated, a 421 mg/l DDT suspension being reduced to 1 ppm after 1 hr reaction at 75°C.

This report was submitted in fulfillment of Contract 14-12-596 between the Federal Water Quality Administration and Aerojet-General Corporation.

Key Words: Pesticide Degradation, DDT, Reduction, Encapsulation, Soil, Water, Chlorinated Pesticides, Polychlorinated Biphenyls.

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*See glossary for formulas of pesticides and degradation products.

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SECTION I

CONCLUSIONS

- The feasibility of controlled, self-destruction pesticides was demonstrated by the effective degradation of DDT using a reductive process with coatings to delay inception of the degradation reaction.

- Degradation of DDT with a mildly acidic reduction by zinc leads to the formation of bis(p-chlorophenyl) ethane, a product from which all three of the aliphatic chlorines in DDT are removed. The reaction was carried out in the laboratory at ambient temperature without forming DDE as a product.

- The mildly acidic zinc reduction of DDT can be effectively catalyzed by copper to give a 2-4 fold faster ambient temperature reaction and an equivalent greater conversion to the bis(chlorophenyl) ethane product. The catalyzed system appears to promote the direct conversion to the ethane product, whereas the uncatalyzed system may proceed by a slower, stepwise dechlorination of DDT.

- Reaction of DDT with mildly acid copper-catalyzed aluminum or iron has led to the formation of a reductive condensation product 1, 1, 4, 4-tetra(p-chlorophenyl)-2, 2, 3, 3-tetrachlorobutane. This hexane-, acetone- and water-insoluble, high-melting-point solid, is reportedly lipoid insoluble and hence would presumably not be transmitted to life forms as a fat soluble species.

- An effective degradation of DDT appears possible in soil by using a micron-sized particle of the reductant in close proximity to the DDT. A 90-95% reduction of the DDT in 4 days was achieved under laboratory conditions by this technique.

- Two techniques appear to hold promise for the controlled delay of the degradation reaction. Thin, slowly-soluble, wax or silyl coatings on the reductant have succeeded in stopping the reaction of micron-sized zinc particles with acid. The second technique which may hold promise for reaction delay involves the slow air oxidation of sulfur to produce required acidity for the reaction *in situ*.

- Although a test of the combined reduction-controlled delay reaction with a DDT-silyl coated, catalyzed zinc system sprayed onto soil did not give the requisite delay because of faulty coating, the fact that a 90-95% reduction of the DDT in soil was achieved is believed to provide ample evidence that the technique will work, given an initially impervious coating.

- Effective degradation of DDT in water has been achieved in suspensions containing as little as 1 mg/l of DDT. Both stirred reactors and packed bed columns were effective in significantly reducing the DDT level of simulated and real DDT-laden waste streams.

- The reductive degradation technique has been found effective in completely or substantially degrading the chlorinated cyclodiene pesticides dieldrin, endrin, aldrin and chlordane; the chlorinated camphene toxaphene; the pesticides related to DDT: Kelthane, methoxychlor and Perthane; the hexachlorocyclohexane pesticide lindane; and selected polychlorinated biphenyls. However, the extent of degradation and the products of the reaction are not known as yet.

- The reductive degradation process appears to be economically feasible, the theoretical cost for zinc powder to reduce DDT to bis(p-chlorophenyl)ethane being about 5.5 cents/lb of DDT, while the cost is calculated to be 1.0 cents/lb or 0.2 cents/lb of DDT if the reductant is respectively catalyzed aluminum or catalyzed iron and the product is the tetra(chlorophenyl) tetrachlorobutane. The simple coating process and materials suggest that the reaction delay process may also be economically feasible. The fact that the DDT-reductant particles can be suspended and sprayed by a conventional air-blast atomizer also suggests practicality of the approach.

SECTION II

RECOMMENDATIONS

This study had as its objective the determination of the feasibility of a concept for the controlled degradation of chlorinated pesticides. With the establishment of the feasibility of this concept, the further development of this important process for the several applications that appear evident from these studies is recommended. These include:

- Development of the process for controlled destruction of field-applied DDT.
- Development of the process for controlled destruction of field-applied chlordane, toxaphene or other chlorinated pesticides of importance.
- Extension of the studies to the treatment of chlorinated cyclodiene pesticide wastes, such as the dieldrin used in wool mothproofing operations.
- Further development of the reductive degradation technique for the treatment of waste effluent or accidental discharge from DDT manufacturing plants.
- Examination of the feasibility of the reductive degradation technique for degrading polychlorinated biphenyls (PCB's), and the development of suitable waste control procedures to be used with PCB's.
- Examine the feasibility of using the reductive degradation technique for cleaning up agricultural fields contaminated with chlorinated pesticides, and for destroying surplus or waste pesticide products.

It will be important in developing suitable degradative techniques to be assured that the products are harmless to life forms, and indeed to know the extent to which the pesticide must be changed in order that it not present a problem to the environment. While acute toxicity data is generally known or can be obtained readily, the chronic or reproductive effects that lead to the "thin-eggshell syndrome" on exposure to DDE or dieldrin are not well understood. This understanding is required for the effective development of pest control agents.

SECTION III

INTRODUCTION

The objective of this study has been the determination of the feasibility of the degradation of persistent chlorinated pesticides to a form harmless to life, with the pesticide detoxification being delayed for a suitable time period so that the pest-control agent could exercise its designed function. DDT was selected as the chlorinated pesticide to be examined in initial studies, although limited tests with other chlorinated pesticides were to be undertaken if time permitted.

Although an initial degradation of DDT to DDE was proposed, it was determined that more complete degradation of DDT without forming DDE as a product was strongly desirable, and the objectives of the study were modified accordingly. The degradation of 80% of the pesticide in one week at ambient temperatures was an initial goal. Delay of the degradation for 15 to 30 days, or until sloughing-off from the plant to the ground, were assumed as target times.

The program as initially set up consisted of five phases: (1) Selection of Detoxification Reagents, (2) Selection of Controlled Delaying Techniques, (3) Laboratory Evaluation of Delayed Pesticide Degradation Reaction, (4) Laboratory Feasibility Examination of Application of Reagents with Spray Formulation, and (5) Evaluation of Concept Feasibility. The early determination that DDE was an undesirable product resulted in primary emphasis on the first task: the study of the basic chemistry of degradation leading to a selection and development of the degradation reagent system.

The selection of the degradation reagents was based on the results of a screening study in which five basic mechanisms of DDT degradation were examined. These five basic techniques included Lewis-acid catalysis, free radical catalysis, oxidation, reduction, and hydrolysis. On the basis of these studies, the reduction technique was chosen for further development, and studies directed towards the development of simple and effective reductive degradation techniques will be described. Application of the technique to reduction of other chlorinated pesticides and to the related polychlorinated biphenyls is also described, as well as studies showing that the reductive degradation of DDT in water and soil can be achieved.

The selection of controlled delaying techniques involved studies with two basic mechanisms of reaction delay. The first involved the use of coatings on a reactive ingredient (such as the reductant) which would be slowly dissolved or eroded from the particle, thus allowing a reaction after a given delay period for pest control action. This is the basic technique employed with many of the "controlled-release" fertilizers (Reference 1). The second basic technique employs a slow reaction to generate an essential ingredient for the reductive reaction.

Limited studies of the delayed degradation of DDT in soils have also been undertaken. These tests have included the reductive degradation of DDT in soils, and tests in which coated reductant was applied to soil along with the pesticide DDT. In some of these tests the pesticide and the reductant were applied simultaneously by a spraying technique; indeed, it will be shown that simultaneous application of the pesticide and degradation reagents is the preferred mode of application.

The analysis of the concept feasibility will be a part of this report.

In the sections to follow, the basic chemistry and experimental results leading to a selection of the reductive technique will be described, the development of the dissolving metal reduction of DDT will be summarized, the discovery that the basic metallic reduction technique can be catalyzed to yield a significantly more rapid and selective process will be described, studies leading to the degradation of DDT in waste waters will be summarized, the results of tests of the degradation of DDT in soil will be given, delayed reaction studies will be summarized, and the tests of the combined application of a delay technique and the reductive degradation process to studies on soil will be described. Data showing that the reductive degradation technique is applicable to chlorinated pesticides other than DDT, and to the related industrial compounds, the polychlorinated biphenyls, will also be given.

SECTION IV

SELECTION OF DEGRADATIVE TECHNIQUE FOR DDT

The initial task of the Aerojet studies under Contract 14-12-596 consisted of the examination of several possible degradative techniques for DDT and from these the selection of the most promising mechanism for the practical destruction of the pesticide. Some of the basic considerations leading to the selection of the optimal means for DDT degradation include:

- Degradation to proceed to the greatest extent possible, removing a significant amount of chlorine from the molecule. The products DDE and DDD were to be avoided if possible. The major products should be harmless to life forms, whether mammalian, fish, or bird life.
- The degradative reaction should proceed to a substantially complete destruction of DDT at ambient temperature (~25°C) in periods of a week or less.
- The reaction should be capable of being carried out in both soil and water, so that detoxification of both of these media may be achieved.
- The degradative technique should be economically feasible, and should not employ difficult to obtain materials.
- The catalyst or degradative materials used should not result in the introduction of harmful materials into the environment.

Basic Chemistry of Degradation of DDT

An examination of the basic chemistry of DDT and other halogenated organic compounds suggested several processes which should be investigated for their feasibility in practically degrading DDT in accordance with the considerations outlined. The reviews published on the chemistry of DDT (e.g., References 2, 3, 4, 5) suggest that the material is a relatively stable moiety, although some techniques are known for its decomposition.

It has been known that the dehydrohalogenation of DDT to DDE could be catalyzed by iron and iron salts, anhydrous aluminum chloride and certain mineral carriers (Reference 6). In studies in which the stability of DDT and other chlorinated pesticides was related to the "surface acidity" of mineral carriers, it became evident that dehydrochlorination was catalyzed by an acidic nature of the carrier surface (References 7, 8). Indeed, these studies suggested a correlation between pesticide stability in contact with mineral carriers and a low surface acidity. Conversely, highly acid surfaces were found to catalyze decomposition, in the case of DDT apparently leading to conversion to DDE. The use of strong Lewis-acid catalysts to promote decomposition was one mode which was selected for evaluation.

The photochemical decomposition of DDT reportedly occurs by a free-radical mechanism (Reference 9). Hence the use of catalysts which promote free-radical reactions might be expected to be useful in effectively degrading DDT, so materials of this type were also evaluated for their efficacy in degrading this pesticide.

Although it has been reported that DDT is relatively stable to reduction, it is known that the molecule can be degraded under rigorous conditions to products other than DDE. For example, Beckman and Berkenkotter (Reference 10) used sodium-liquid anhydrous ammonia system to dechlorinate DDT, giving 1,1-diphenyl ethane as the product. Reduction by sodium in refluxing isopropanol with subsequent titration of the chloride is a standard method for DDT analysis (Reference 11). Less rigorous conditions for reduction were suggested by Hornstein (Reference 12), who found that by passing DDT through a zinc column, a 50% reduction of the chlorine content could be realized. In another study, Romano (Reference 13) reported the reduction of three of the five chlorine atoms on DDT by refluxing an alcoholic-kerosene solution of DDT with ammonium sulfate and zinc. Although these procedures suggest that DDT may be reduced without forming DDE as a product, it remained to be determined that the reaction would proceed in a practical way at ambient temperatures without employing columns, exotic reagents, or other conditions which would negate a practical field-applied degradation process. Clearly, further studies were required to determine the feasibility of a practical reductive attack of DDT.

The dehydrohalogenation of DDT by base is well known and has been used extensively for the analysis of DDT. The kinetics of alkaline hydrolysis have been investigated by many workers (e.g., Cristol, Reference 14). It has also been determined that basic amines are capable of extracting an HCl molecule from DDT to give DDE (Reference 15). Although the simple removal of one HCl from DDT is generally assumed on alkaline hydrolysis, Grummitt, Buck and Stearns reported that elevated temperature hydrolysis under severe conditions leads to the formation of the bis (p-chlorophenyl) acetic acid, DDA (Reference 16). Accordingly, limited experiments were conducted in order to determine if the hydrolysis reaction of DDT could be made to proceed readily to an end product other than DDE.

It is well known that the body converts DDT to the soluble acetic acid derivative, DDA (bis(p-chlorophenyl) acetic acid) (Reference 17). Hence a brief examination of oxidizing techniques for the degradation of DDT were considered.

In summary, it will be shown that the reductive technique is preferred for effective ambient temperature degradation of DDT without forming DDE as a product. The results of the screening tests are summarized in Table No. 1; the details of the tests will be presented in the sections to follow. Available information on the toxic properties of some important products of the reaction are also given; these data appear to substantiate the selection of the reductive degradation of DDT to yield bis (p-chlorophenyl) ethane as a product which would appear to be without the toxic effects of DDT. The data from the screening tests will be grouped according to the type of reaction which was investigated.

The principle product analysis has been by gas chromatography. The methods of analysis and identification of product peaks are described in Appendix A.

TABLE 1

SUMMARY OF SCREENING TESTS OF DDT DEGRADATION

LEWIS ACIDS:	
$AlCl_3$, $AlBr_3$	- extensive degradation at 25, 50, 100°C. DDE a substantial product.
$FeCl_3$	- less effective than $AlCl_3$.
Clays, halide salts	- generally ineffective.
REDUCTION:	
Zn + dil acetic acid	- complete degradation of DDT without DDE as a product. Reaction proceeds at 25°C.
Zn + $(NH_4)_2SO_4$	- degradation as with acetic acid but slower at 25°C.
FREE RADICAL:	
Benzoyl peroxide	- complete conversion to DDE at 100°C; little reaction at lower temperatures.
Other peroxide catalysts	- none effective at ambient temperature.
Redox system	- substantial 25°C conversion to DDE.
OXIDATION:	
Hot chromic acid (117-120°C)	- slow reaction; 40% DDT reacted in 8 hr.
$KMnO_4$	- little reaction at 25°C.
ALKALINE HYDROLYSIS:	
KOH - ethanol	- essentially complete conversion to DDE at 78°C.
KOH - n-butanol	- conversion to DDE and other products at 117°C.
KOH - ethylene glycol	- complete consumption of DDT at 168-175°C, mainly giving unidentified products.

SCREENING TESTS

Lewis-Acid Catalysts

An extensive investigation of the applicability of strong Lewis-acids as catalysts for DDT degradation was made. This decision was predicated on the observation that certain mineral fillers and metal halide salts were known to catalyze the degradation of DDT, but the practical extent of reaction was not known. If a clay-like catalyst, for example, could be found which promoted degradation of DDT to desired end products, a system would be provided which would satisfy the requirements for a process which would not add harmful materials to the environment.

In the discussion to follow, data will be presented in which the metal halides and metal halide hydrates, modified montmorillonite catalysts, commercial clay catalysts, and some BF_3 adducts were examined as catalysts. Data will also be shown on the effect of a solvent on the reaction (most of the tests were conducted on dry mixes of DDT and the catalyst), and a correlation with the Hammett acidity will be presented.

$AlCl_3$

Anhydrous aluminum chloride is a well-known catalyst for a variety of organic reactions reportedly effective in degrading DDT* (Reference 6). The $AlCl_3$ was ground in an agate mortar before blending, the DDT was added and the samples were blended by grinding in the mortar for 5-10 minutes. These operations were conducted in a dry box, because of the affinity of anhydrous $AlCl_3$ for water.

Samples weighing about 1 g were placed in 16 x 150 mm glass-stoppered test tubes and were heated in a thermostatted, stirred oil bath at 100°C for 2 hr. After less than 5 min reaction, the evolved gases blew the stopper from the test tube and the reaction mass turned to a black char. The sample was removed from the bath after 2 hr, cooled, and the mass dissolved in benzene. The black char dissolved very slowly and the resultant solution was colored red. A black residue which was soluble in water, although insoluble in benzene, was filtered off; the residue

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* The DDT used in these experiments was purified by recrystallizing from absolute ethanol twice; mp 108.6-108.8°C. In this report, the term DDT indicates purified p,p'-DDT unless otherwise stated.

appeared to be $AlCl_3$. The gas chromatographic analysis of the solution was as follows:

Component	Gas Chrom. Retention Time, Min.	%*
DDE	15.2	26.3
	16.3	57.5
DDD	17.8	13.7
DDT	21.0	1.0
	28.8	1.3

It is important to note that essentially all of the DDT was decomposed under these conditions. Although a substantial amount of DDE was obtained, two additional unidentified peaks accounting for 59% of the observed decomposition were obtained. One attempt was made to identify these peaks by trapping gas chromatographic effluent with a given retention time range and subjecting the material to mass spectral analysis. The DDE peak was confirmed but other peaks were not identified.

The ambient temperature decomposition of DDT by $AlCl_3$ has also been observed. When DDT was ground with 10wt. %$AlCl_3$, an immediate coloring of the mix was obtained. An analysis of the mix after approximately 2 days and 1 week reaction at 25° follows:

Product**	Retention Time, min	Analysis, %, after Reaction, hr, at 25°C	
		45	166
DBP	9.8	-	1.8
	14.2	-	5.3
DDE	15.1	0.7	48.9
	16.4	5.0	16.0
DDD	17.6	28.6	-
	19.0	5.4	-
DDT	21.0	56.3	15.0
	23.4	-	0.3
	27.6	-	4.3
	28.5	-	0.7
	29.3	-	1.2
	31.2	1.0	-
	32.4	0.7	-
	34.4	-	1.0
	37.9	<0.7	0.3
	40.9	<0.7	5.1
	42.3	1.0	-
	44.4	1.2	-
	47.4	-	0.3

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* Analysis based on the calibration curve for DDT; the sensitivities for other materials with retention times in the range cited will be approximately the same as DDT.

**See Glossary for names and chemical formulas of products.

The sample experienced a weight loss (presumably HCl) of 7.3% over the 166-hour reaction period.

Several general conclusions can be made. First, the gas chromatographic analysis indicates a large number of degradation products so that substantial degradation beyond DDE is being obtained. Secondly, decomposition of the DDT at room temperature in reasonable periods of time was achieved with this strong Lewis-acid type catalyst.

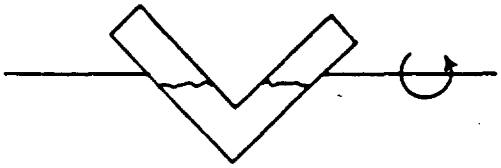
A comparison of the overall rate of DDE appearance and DDT removal can be made.

	45 hr	166 hr
Rate of DDE appearance, %/hr	.64	.30
Rate of DDT removal, %/hr	.97	.51

The sensitivity of the aluminum chloride to moisture was shown when material which was stored in a presumeably dry atmosphere was found to rapidly loose its activity, yet a freshly-opened bottle of the anhydrous aluminum chloride reproduced the preceding data.

It was observed in carrying out the reactions that extensive mixing of the samples in the mortar and pestle would produce dark "reaction-zones", where immediate reaction was obtained. In an effort to separate the $AlCl_3$-catalyzed reaction from possible localized heating effects, a means for sample mixing which did not require grinding of the mixed samples was investigated.

A small "V" shaped particle blender was constructed of glass, the two arms of the blender being 1 cm dia by 4 cm long. The "V" blender was turned by a small motor at a rate of 20 RPM. This blender is a scale-down of a commercial type particle blender; a unit of this type had been used previously by the investigators for efficient mixing of small, fine-particle blends.



When samples of finely-ground $AlCl_3$ and DDT were mixed in the blender, it was found that reaction was initiated at ambient temperatures. However, two important observations were made. First, sample darkening indicative of reaction appeared most extensive at areas on the reaction tube where relatively high concentrations of the catalyst were evident; this observation had also been made previously when extensive darkening of a sample appeared to initiate in fine dust located on the sides of the reaction tube. Secondly, progressive darkening appeared to spread from small dark reaction sites in the mix. Thus autocatalysis must be considered.

In an effort to further characterize the effect of $AlCl_3$ mixing and concentration, a sample consisting of DDT, 1% $Ca_3(PO_4)_2$ added to promote free-flowing properties, and 29.1% anhydrous $AlCl_3$ was prepared. The mixture turned brown immediately upon mixing and soon tended to be "sticky" in texture. Within 1 hr at 25° the reaction mix turned a dark purple color. The mix was allowed to react for 116 hr at 25°C. The weight loss after this time was 15.7%. The results of the analysis of the reaction mix follow:

Component	Retention Time, min	Reaction 116 hr at 25°C, %
	1.6	0.3
	10.4	0.9
	13.4	0.1
	14.8	2.5
DDE	15.6	10.8
	17.0	18.4
DDT	21.4	0.1
	22.2	0.3
	28.4	3.7
	35.4	0.7
	40.4	0.4
	42.0	1.0

The analysis does not account for 61% of the sample. However, thin-layer chromatography results indicate that DDA may be a major product; DDA will not respond in standard gas chromatography.

These results show that DDT may be degraded by $AlCl_3$, but the material is highly moisture-sensitive. Further, DDE is a significant product. A large number of other products, mainly small quantities, are obtained.

$AlCl_3$ Hydrate

In an effort to establish that the aluminum chloride catalysis is due to a strong Lewis-acid rather than an effect specific to $AlCl_3$, an experiment was also conducted with the hydrate of $AlCl_3$, since the water is a strong Lewis base. The results of reaction of DDT with 10% ($AlCl_3$ anhyd. basis) of $AlCl_3 . 6H_2O$ for 2 hr at 100°C follow:

Component	Retention Time, Min.	%
	12.1	trace
	13.3	trace
DDE	15.4	1.5
DDT	21.0	98.5

Thus the hydrate of $AlCl_3$ was ineffective in promoting DDT decomposition.

$AlBr_3$

A recent analysis of the Lewis-acidity of covalent metal halides by Satchell (Reference 18) suggests that $AlBr_3$ should be a stronger Lewis acid than $AlCl_3$. A sample of the material was therefore procured and its reactivity with DDT was examined.

In the experiment, 1 g of recrystallized DDT was mixed with 12% by weight of $AlBr_3$ in the "V" mixer. The ingredients immediately became black and sticky. The mix was transferred to a mortar and blended with a spatula without grinding. After 15 min at 25°, the mix was dissolved in benzene, filtered and analyzed. The results follow:

Component	Retention Time, Min	Analysis, %, after 15 min Reaction at 25°C
DBP	10.1	0.1
	12.2	0.2
DDMU	13.1	1.2
DDMS	14.5	1.8
DDE	15.6	22.5
	16.8	5.5
DDD	18.1	0.6
	19.0	6.3
DDT	21.0	26.6
	21.8	5.0
	24.8	0.3
	28.8	0.4
	29.8	0.5
	32.2	<0.1
	35.1	0.2
	36.8	0.2
	39.8	0.7
	41.8	2.9

Approximately 25% of the products were not found in the gas chromatographic analysis and may represent products which will not elute from the column under the conditions employed (DDA and p-chlorobenzoic acids, for example). It is clear that very substantial degradation of the DDT was obtained with $AlBr_3$ catalyst, leading to a large number of products. The reaction was rapid, too, since a 74% destruction of DDT occurred in 15 min at room temperature. However, $AlBr_3$ is very hygroscopic and loss of activity would be expected after brief exposure to moisture-laden air.

$FeCl_3$

Anhydrous ferric chloride has been reported to be effective in DDT decomposition, similar to $AlCl_3$ (Reference 6). Indeed, the results with 10% by weight of anhydrous ferric chloride resemble those with aluminum chloride in that a strong reaction leading to a charred reaction mass was observed after less than 5 min reaction at 100°C. After 2 hr reaction the mass was dissolved in benzene, yielding a dark green solution. A tan-white insoluble residue (6.3% of the DDT weight) was filtered off; the residue (probably $FeCl_3$ or $FeCl_2$) was water soluble. The analysis of the benzene solution was as follows:

Reaction of DDT with 10% $FeCl_3$ for 2 hr at 100°C

Component	Retention Time, Min.	%
	14.7	12.8
DDE	16.0	81.8
	16.9	5.0
DDT	21.3	0.2
	25.7	0.1

Thus, DDT was essentially completely decomposed under these conditions, with approximately 80% of the material being present as DDE and 20% apparently as the same two unidentified products which were obtained when $AlCl_3$ was employed as a catalyst.

The reaction of DDT with 10% by weight of anhydrous $FeCl_3$ was also studied at 25°C. The results after nominal 1-day and 5-day reaction follow:

Component	Retention Time, min	Analysis, %, after Reaction, hr, at 25°C	
		24	116
	12.6	0.1	0.1
	15.0	0.3	0.8
DDE	15.7	3.5	9.8
DDD	18.8	0.1	0.4
DDT	21.3	95.7	84.3
	29.8	-	0.1
	30.3	-	0.2
	33.0	0.4	3.5
	35.4	-	0.5
	43.6	-	0.5

In another test in which the $FeCl_3$ had apparently absorbed some moisture from the air, a 45 hr reaction of DDT with 10% by weight of $FeCl_3$ resulted in 94.8% of the DDT being unreacted with 5.2% being present as DDE. After 166 hr, the DDT assayed 92.7%, while 6.8% was DDE.

Thus, reaction of DDT with $FeCl_3$ at ambient temperature appears to proceed much more slowly than with $AlCl_3$.

$FeCl_3$ Hydrate

A result similar to that obtained with aluminum chloride hydrate was obtained when $FeCl_3 \cdot 6H_2O$ was used in an attempt to catalyze DDT decomposition. The amount of the salt was adjusted to contain the same concentration of $FeCl_3$ as was used in the anhydrous salt reaction.

Component	2 hr Reaction of DDT + 10% (anhyd basis) $FeCl_3 \cdot 6H_2O$ at 100°C	
	Retention Time, min	%
	13.2	<0.5
DDE	15.4	2.0
DDT	20.7	98.0

Protonated Montmorillonite

A siliceous material which reportedly has a high surface acidity and hence might be expected to degrade DDT is the protonated form of montmorillonite clays. The process for preparation of the material is basically that employed by Dr. G. W. Bailey of the Southeast Water Laboratory, FWQA (Reference 19).

Montmorillonite from Upton County, Wyoming (Ward's No. 25) was separated as a < 2 μ fraction by sedimentation in water. The fine fraction was air dried and then heated at 240°C overnight. The montmorillonite was then converted to the acid form by slowly passing a 1% suspension of the clay through an acid-form Amberlite IR-120 ion exchange column. The material was passed through the 48 mm dia x 50 cm long column at a rate of 2 ml/min. The effluent was then centrifuged to separate it from the bulk of the water and freeze-dried (product temperature -10 to -20°C, ~ .5 mm pressure). The material was stored at dry ice temperatures overnight until use.

A 10% mixture of the acid form montmorillonite was reacted with DDT for 2 hr at 100°C. After that period of time the mass had darkened appreciably and a 0.22% weight loss was obtained. The benzene solution was yellow colored; however, analytical data for the initial experiment show that no significant decomposition had occurred.

Component	Retention Time, min	Reaction 2 hr at 100°C, %
DDE	15.4	3.4
DDT	20.6	96.6

A further attempt to catalyze DDT decomposition with the protonated montmorillonite was made when a new batch of the montmorillonite was converted to the acid-form, freeze-dried, and the reaction run in a single day so that stability considerations could be minimized.

The montmorillonite was converted to the acid form by slowly passing it through a freshly regenerated IR-120 ion exchange resin, using the same procedure as outlined previously. The pH of the effluent acid-form montmorillonite suspension was 2.50. After the material was freeze-dried, the surface acidity was determined with Hammett indicators. The material gave a strong, yellow coloration with the benzalacetophenone indicator (pK_a -5.6), but did not give a color with anthraquinone (pK_a -8.2), giving a pK_a for the material between -5.6 and -8.2. The results of a test in which 10% of the freshly prepared protonated montmorillonite was reacted with DDT for 2 hr at 100°C yield the following analytical results:

Component	Retention Time, min	Reaction 2 hr at 100°C, %
	14.8	0.2
DDE	15.6	5.2
	17.0	0.3
DDT	21.4	88.3

Clearly, significant decompositon of DDT was not obtained with this catalyst.

Copper Montmorillonite

Montmorillonite in which copper has been added by ion exchange has also been prepared for evaluation as a DDT degradation catalyst.

A portion of the air-dried < 2μ fraction of montmorillonite (Ward's No. 25) was reacted repeatedly with cupric chloride. The montmorillonite was treated with $CuCl_2$ solution at the rate of 3 ml of 1 N $CuCl_2$ solution per g of air-dried clay. If the montmorillonite has an exchange capacity of 0.3 meq/g, then the $CuCl_2$ was added in nine-fold excess. The clay-$CuCl_2$ solution was shaken for 30 min with a wrist-action shaker, centrifuged, and the $CuCl_2$ solution decanted off. A fresh portion of $CuCl_2$ was added, the clay re-suspended and shaken for an additional 30 min. The process was repeated for five 30-min periods, each with a nine-fold excess $CuCl_2$. The product was then washed with distilled water by suspension, and centrifugation, until the liquid was free of chloride (by silver nitrate precipitation).

The copper montmorillonite was employed in a test in which 10% of the catalyst was reacted with DDT for 2 hr at 100°C. The analytical data, which indicate little decomposition of the DDT, follow:

Component	Retention Time, min	Reaction 2 hr at 100°C, %
	14.8	0.2
DDE	15.6	8.0
	17.4	<0.1
	18.9	0.5
DDT	21.1	91.4

Silica-Alumina Catalysts

Silica-alumina catalysts are reported to be effective for catalytic cracking with the catalytically active sites identified as acid centers

(Reference 20). A series of these experimental silica-alumina catalysts was obtained from the Houdry Process and Chemical Company. Reported characteristics of the catalysts tested follow:

Catalyst	2 CP 13	523 CP 8
Surface area, m^2/g	375-400	180-200
Porosity, vol %	60	56
Absorption, wt %	65	55
Avg. Pore Diameter, A	80	85
Al_2O_3, wt %	12.4	12.4
SiO_2, wt %	87.3	87.3
Na_2O, wt %	<0.25	<0.25

These catalysts were obtained as small pellets which were ground in an agate mortar to a fine powder and dried at 110° overnight. The results of a test in which 10% of each of these catalysts was blended with DDT and reacted for 2 hr at 100°C gave the following analytical results:

		Reaction 2 hr at 100°C	
		Product Analysis, % with Catalyst	
Component	Retention Time, min	2 CP 13	523 CP 8
	14.8	0.1	0.1
DDE	15.6	5.7	3.4
DDD	17.4	<0.1	-
	18.9	<0.3	0.5
DDT	21.1	93.8	96.0

These results indicate no significant decomposition of DDT under the conditions employed.

Commercial Clay Cracking Catalysts

Two commercial clay-type catalysts have been evaluated and have been found ineffective in promoting degradation of DDT.

One of the materials evaluated was Filtrol type F-13. This material is an activated clay with reported high acidic properties. The surface area (BET) is rated at 325 sq m/gm and the acidity is given at 16 mg KOH/gm. Initial tests with DDT showed no difference from the DDT control when a mixture was heated for 2 hr at 100°C. The data in a test using 10% of the as-received clay as a catalyst follow:

	Reaction 2 hr at 100°C	
Component	Retention Time, min	%
	12.9	0.7
DDE	15.1	1.1
DDD	17.9	<0.5
DDT	20.7	98.3

On contacting the supplier, an activating treatment of heating to 240°C for 4 hr was suggested. The results of a test in which 10% of the activated catalyst was used follow:

Component	Retention Time, min	Reaction 2 hr at 100°C, %
	12.0	<0.5
	13.2	<0.5
DDE	15.4	2.0
DDD	18.3	<0.5
DDT	21.1	99.0

The second clay catalyst purported to have a high surface acidity was supplied by Georgia Kaolin Company. This material, termed Hydrite UF, was believed to be a kaolinite-type material. Reaction of 10% of -325 mesh material with DDT follows:

	Reaction 2 hr at 100°C	
Component	Retention Time, min	%
	12.5	<.5
	13.5	<.5
DDMS	14.2	<.5
DDE	15.7	3.3
	16.6	<.5
DDD	18.4	<.5
DDT	21.0	96.7

Clearly, these materials have promoted no substantial degradation of DDT.

Acid -Form Exchange Resin

On the basis that strong surface acidity may catalyze DDT decomposition, a reaction of finely ground acid-form Amberlite IR-120 resin with DDT was attempted. The finely ground material was dried over Drierite in vacuum before use. When the DDT was heated with 10% by weight of IR-120 for 2 hr at 100°C, neither a coloration of the mass nor a weight loss were obtained. The benzene solution was also colorless. Analysis of the sample showed no substantial degradation:

Component	Retention Time, min	Reaction 2 hr at 100°C, %
	12.6	<0.1
DDE	15.7	2.1
DDD	18.8	<0.1
DDT	21.3	98.4

On the basis that the lack of catalytic activity might be attributed to moisture, a comparison was made in further experiments between mixes prepared from the IR-120 resin dried in an oven at 110°C for 16 hr, and material dried in a vacuum desiccator over Drierite for

16 hr. In both cases 10% of the resin was mixed with the recrystallized DDT and reacted for 2 hr at 100°C. The analytical results indicate little decomposition of the DDT.

Component	Time, min	Reaction 2 hr at 100°C Product Analysis, % When Catalyst Oven dried	Reaction 2 hr at 100°C Product Analysis, % When Catalyst Vacuum desiccator dried
	12.4	0.1	<0.1
	14.8	0.2	0.4
DDE	15.6	6.0	7.3
	17.4	0.1	0.2
	18.9	0.4	0.7
DDT	21.1	93.0	93.8

BF_3 - Adducts

A general consideration of Lewis-acid theory leads one to BF_3 and its adducts, as compounds with high Lewis-acidity (Reference 18, 21). In particular, the adduct $BF_3 . H_3PO_4$ has been used as a catalyst in some organic reactions where correlations with Lewis-acidity were noted (Reference 22). Accordingly, the $BF_3 . H_3PO_4$ adduct was prepared and its catalytic activity with DDT determined.

The $BF_3 . H_3PO_4$ (+ BF_3 hydrate) was prepared by the method of Axe (Reference 23). The method consists of the saturation of 85% H_3PO_4 with BF_3, forming the liquid catalyst. In a comparative test, a catalyst consisting of o-dichlorobenzene saturated with BF_3 was also employed. The results of the analyses of the products of DDT reaction with these catalysts at 25° and 100°C follow. In each case, 1 ml of catalyst was used with 1 g of DDT.

Component	Retention Time, min	Analysis, %			
	Catalyst:	$BF_3 . H_3PO_4$		$BF_3 . H_3PO_4$ o-dichloro-benzene solvent	BF_3-satd. o-dichloro-benzene solvent
	Reaction:	120 hr; 25°	2 hr; 100° 118 hr;25°	2 hr; 100° 118 hr;25°	120 hr;25°
	14.2	0.1	0.1	0.1	0.1
DDE	15.6	10.8	16.5	10.3	9.5
	19.0	<<0.1	<<0.1	<<0.1	-
DDT	21.4	89.0	83.3	89.7	89.3

Clearly, little reaction was shown, with the only significant product being DDE. This catalyst system therefore holds little promise.

Solvents

Early degradation studies on DDT by Fleck and Haller (Reference 24) indicated that the catalytic action of $FeCl_3$ was promoted by solution in selcted chlorobenzenes, chloronaphalene, and nitrobenzene, and inhibited by various hydrocarbon and fatty oils, alcohols, ketones, etc. The solvent which appeared to give the greatest degradation with $FeCl_3$ and DDT was o-dichlorobenzene. Accordingly, experiments were carried out in order to determine whether this solvent would aid degradation of DDT by siliceous catalysts, as well as $FeCl_3$. In these experiments, 1 g of DDT and 1 ml (ca. 1.3 g) of distilled o-dichlorobenzene were reacted with the given catalysts; the results follow:

		Analysis, %			
	Catalyst:	$FeCl_3$	Protonated montmorillonite	Copper montmorillonite	Houdry* 24CP12
	Catalyst, %:	0.42	13.3	14.6	38.0
	Reaction:	1 hr, 100°C	2 hr, 100°C	2 hr, 100°C	2 hr, 100°C
Component	Retention Time, min				
	12.2	-	-	0.1	-
DDMU	13.1	-	0.1	0.1	-
DDMS	14.5	13.1	-	0.5	-
DDE	15.6	83.2	15.6	32.1	17.2
	16.8	7.6	-	0.1	-
DDD	18.1	-	0.3	0.8	-
DDT	21.0	-	86.6	66.5	74.2

The use of a solvent has increased the extent of reaction obtained, especially with the siliceous catalysts. However, DDE appears to be the principal product.

Surface Acidity Correlation

It has been suggested in earlier works (e.g., Reference 8) that decomposition of DDT catalyzed by clays could be correlated with the surface acidity or Lewis-acid response as shown by Hammett indicators. Experiments to determine the surface acidity response of some of the materials investigated were carried out in an effort to determine useful correlations.

The indicators were dried in a vacuum desiccator over Drierite and were prepared as 0.1% solutions in benzene dried over fresh P_2O_5. The indicator solutions were stored in a desiccator.

The procedure employed and the indicators employed were essentially as described by Benesi (Reference 25). An approximately 0.1 g portion of the sample was transferred to a 5 ml glass vial and 3 ml of dry

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* A silica alumina catalyst having a specific surface of 425-450 m^2/g, an average pore diameter of 70 A, and containing 12.4% Al_2O_3, 87.3% SiO_2, and 0.25% Na_2O.

benzene (dried overnight over fresh P_2O_5) added. The indicator solution was then added and the suspension shaken. The indicators and their pKa follow:

A.	Phenylazonapthylamine	+4.0
B.	Butter Yellow	+3.3
C.	Benzeneazodiphenylamine	+1.5
D.	Dicinnamalacetone	-3.0
E.	Benzalacetophenone	-5.6
F.	Benzoylbiphenyl	-6.2
G.	Anthraquinone	-8.2
H.	Picramide	-9.3

The results obtained with selected samples follow:

Catalyst	Indicator	Color	Indicator	Color	pKa
Filtrol F13					
as received	E	yellow	G	colorless	-5.6
dried 240°C	E	yellow	G	colorless	-5.6
Hydrite UF	E	yellow	G	colorless	-5.6
Acid Montmorillonite	E	yellow	G	colorless	-5.6
Montmorillonite air dried	A	blue violet	B	yellow	+4.0
$AlCl_3$, Anhydrous	G	yellow	H	-	-8.2
$AlCl_3.6H_2O$	A	blue violet	B	yellow	+4.0
$AlBr_3$Anhydrous	G	yellow	H	-	-8.2

The only catalysts tested which were effective for the ambient temperature degradation were $AlCl_3$ and AlB_3, and these materials have the most strongly acid pKa of the materials tested. The sharp decrease in Lewis acidity comparing anhydrous $AlCl_3$ with the hydrate (-8.2 vs +4.0), and the modest decrease in pKa apparently necessary in order to effectively stop degradation (catalyst effective at pKa -8.2, catalysts at -5.6 not effective) would show clearly why the absorption of a small amount of moisture would make the anhydrous metal salts ineffective as catalysts.

Summary

In summary, the strong Lewis acid catalyst $AlCl_3$ has shown the ability to degrade DDT, even at ambient temperatures. Although one product is DDE, other products in substantial quantities are obtained. Similar results were obtained with $AlBr_3$, substantially degrading DDT in a few minutes at ambient temperature. However, the adsorption of small amounts of moisture appears to seriously decrease the effectiveness of the catalyst, and the addition of water, a strong Lewis base, to form the hydrate leads to essentially no degradation of the DDT. Anhydrous ferric chloride also catalyzes decomposition of DDT, but the reaction appears less extensive at ambient temperatures than is obtained with $AlCl_3$. The clay and modified montmorillonite catalysts have not been effective in catalyzing DDT decomposition. The use of acid form exchange resin and BF_3 adducts has also led to ineffective catalysis of DDT degradation. The use of the solvent o-dichlorobenzene leads to substantially greater degradation of DDT by the protonated montmorillonite, copper montmorillonite, and a commercial alumina-silica catalyst, but DDE was the principal product.

Reduction

The mildly acidic reduction of DDT by zinc was investigated for its efficiency in reducing DDT. Highly promising results were obtained which led to its selection as the technique most suitable for development as a practical degradation process that might be used for both field and waste system treatment of DDT.

The initial test was made using an adaptation of the acidic reduction system used by Romano (Reference 13). In this study, 1 g of DDT was dissolved in 50 ml of alcohol, and 2 g of $(NH_4)_2SO_4$ and 1 g of powdered zinc dust were added and the reactants held at 50°C. Two samples were tried, using 96% or 100% alcohol as the solvent. The results show clearly that substantial reaction occurs in the 96% alcohol, while the 100% alcohol solution was much less effective. The analytical results from these tests follow:

		Reaction 116 Hours at 50°C	
	Retention	96% Alcohol Solution	100% Alcohol Solution
Component*	Time, Min.	%	%
DDEt	8.0	43.7	5.2
	12.4	<0.1	0.1
DDMU	13.4	0.2	0.4
DDMS	14.5	6.8	1.3
DDE	15.8	8.3	10.2
	16.9	-	0.8
DDD	18.0	14.1	7.5
DDT	21.0	26.7	75.4

It is important to note in the test with the 96% alcohol that although more than 73% of the DDT was destroyed, only 8% went to DDE and about 65% formed degradation products other than DDE.

In a further test, the Romano experiment (Reference 13) was carried out over a range of reaction times ranging from 1 hour to 8 hours.

In this study, 1 g of DDT was dissolved in 40 ml of n-dodecane (Romano used kerosene). To this was added 20 ml of 95% ethanol containing 2 g of zinc dust and 4 g of $(NH_4)_2SO_4$, and the resultant mix was refluxed at 78°C. After given times, a 10 ml sample was withdrawn for analysis and 10 ml of a 2:1 dodecane-ethanol mix added to maintain the volume at the initial level.

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* See Glossary for chemical names and formulas of cited compounds.

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 78°C			
		1	2	4	8
DDEt	7.8	72.6	74.3	81.9	81.3
	12.0	0.1	<0.1	<0.2	<0.2
DDMU	13.2	0.7	0.7	0.5	0.7
DDMS	14.2	6.2	6.5	7.5	11.2
DDE	15.4	1.1	-	-	-
	16.3	0.7	<0.1	<0.2	<0.2
	17.4	-	-	0.2	0.7
DDD	17.8	18.5	18.3	9.9	6.1
DDT	21.0	-	-	-	-

Several significant results were obtained from this series of experiments. It is noteworthy that complete destruction of the DDT was found over the complete time range examined, and that DDE was not a product of the degradation (other than the 1.1% found in the 1-hour sample). The significant product was identified subsequently as DDEt, a product from which all 3 aliphatic chlorines have been removed. It is to be noted that this component increases with prolonged reaction.

It would appear that a reduction of DDT should proceed through DDD (the dichloroethane equivalent of DDT) and DDMS (the monochloroethane derivitive), at least as transient species.

It should be noted that the amount of DDD decreased with continued reaction ranging from 18.5% after 1 hr to 6.1% after 8 hrs. The DDMS increased from 6.2 to 11.2% and the DDEt from 72.6 to 81.3% in the same period.

An examination of the literature pointed out another type of zinc reduction which was investigated. Hornstein (Reference 12) used a zinc column in which selected chlorinated pesticides in acetone-dilute acetic acid solution were completely or partially reduced at ambient temperatures. The technique was described as an analytical method for certain chlorinated pesticides.

It was not known, however, whether the zinc reaction could be effectively carried out with a smaller ratio of reductant to DDT than the overwhelming excess to be found in a column. A test was therefore made in which 1 g of DDT was reacted with 1 g of zinc dust. The DDT was dissolved in 20 ml of acetone and 10 ml of 10% acetic acid was added to provide the acidity. This ratio of zinc to DDT provides a 10% excess for reaction to remove all chlorines, and assuming no reaction with the acid. The mixture was reacted for 3 hours at ambient temperature, filtered and analyzed to give the following data:

Component	Reaction 3 Hours at 25°C Retention Time, min	%
	6.0	1.0
DDEt	8.0	20.8
	10.3	0.4
	12.4	0.2
DDMU	13.6	3.2
DDMS	14.5	10.2
DDE	15.8	0.2
DDD	18.0	37.0
DDT	21.0	6.1

These data show that essentially all of the DDT has been consumed, and that DDE was not a significant product. The product with a retention time of 8.0 min, DDEt, appears prominently, as well as DDD.

The promising results of this study were confirmed in other tests; the results of these tests are conveniently grouped in a later section where the development of the mildly acidic reduction of DDT is described at length.

In summary, reduction of DDT with zinc under mildly acidic conditions has given complete or near complete degradation of DDT without forming DDE as a product. The reaction was found to proceed effectively at 25°C in periods of the order of a few hours, yielding a product DDEt (bis (p-chlorophenly)-ethane) which appears, on the basis of published information to be described in a later section of this document, to be "void of the neurotoxic effects of DDT." The reaction employs commonly available materials and the method appears to be economically feasible. The small amount of zinc employed in the reduction may not be deleterious to practical use in the field or in waste treatment of DDT-laden waters. Hence this process was selected for further investigation and development.

Free-Radical Catalysis

Selected free-radical catalysts were investigated for their efficacy in decomposing DDT to preferred end products.

Benzoyl Peroxide

In an initial test, benzoyl peroxide was employed. Finely powdered benzoyl peroxide (10%) and DDT were blended by gentle stirring and heated at 100°C. After about 5 min reaction, the mass melted to form a yellow colored solution. The analysis after 2 hr reaction was as follows:

Component	Reaction 2 Hour at 100°C Retention Time, Min.	%
DDE	15.5	94.1
DDT	20.4	1.3
	25.6	1.4
	29.4	<0.5
	30.3	<0.5
	36.1	1.8

Thus, almost complete decomposition of the DDT occurred, although the degradation was mainly to DDE.

ince the benzoyl peroxide appeared to rapidly catalyze the decomposition DDT at 100°C, an attempt was made at decomposing DDT at 50°C with this material. In a test in which 10% of the catalyst was employed, the following analytical data were obtained:

Component	Reaction 116 Hours at 50°C Retention Time, Min.	%
	1.4	0.2
	4.0	0.2
DDE	15.8	4.1
	18.8	0.4
DDT	21.0	92.7
	36.4	0.8
	41.0	1.5

Substantial decomposition at 50°C was not obtained, although the previously reported decomposition in 2 hours at 100°C was confirmed in another experiment.

Potassium Persulfate

The observation that benzoyl peroxide appeared to catalyze decomposition of DDT to (mainly) DDE suggested the possibility that the decomposition may have been induced by the peroxide function. As a check of this possibility, a sample was run in which DDT was reacted for 2 hours at 0°C with 10% potassium persulfate. Little or no reaction appeared to ve taken place.

Component	Reaction 2 Hours at 100°C Retention Time, Min	%
DDE	15.2	3.9
DDT	20.7	96.1

Azobis Isobutyronitrile

The action of free-radical catalysts was further explored in a test using 2,2' azobis (2-methylpropionitrile). This material was of special interest because (1) the catalyst generally functions at lower temperatures than benzoyl peroxide and (2) the catalyst is not a peroxide but a nitrogen-forming system. Tests were run in which DDT was reacted with 10% of the azobis catalyst at 100° and at 50°C. No substantial decomposition was shown in either case. The analytical data follow:

Component	Reaction Conditions 2 Hours at 100°C	 24 Hours at 50°C
DDE	1.4	1.4
DDT	98.6	98.6

Redox System

An experiment was also carried out in which the redox system commonly used as a free-radical catalysis system for near ambient temperature polymerization was employed. The catalyst system used was basically that given by Marvel (Reference 26).

In this test, 1 g of DDT was dissolved in 10 ml of benzene and added to a solution in which 5 g of Triton X-100 surfactant, 0.5 g benzoyl peroxide, 1.25 g ferrous ammonium sulfate hexahydrate and 1.1 g of potassium pyrophosphate were dissolved in 100 ml of water. The mixture emulsified readily. The mixture was allowed to react for 1 week at 25°C, with frequent shaking. After that time, the DDT and degradation products were extracted repeatedly with benzene and analyzed by gas chromatography. The analyses, which show almost complete destruction of the DDT, has given DDE as a major product, but substantial degradation to other products (~30%) is also shown. The results follow:

	Reaction 168 Hours at 25°C	
Component	Retention Time, Min	%
	1.0	1.3
	1.3	0.4
	1.4	0.4
	2.3	≪0.1
	2.5	<0.1
	3.4	0.3
	3.6	2.9
	8.4	1.5
	11.8	0.3
	13.4	15.1
DDE	15.6	61.0
	18.2	4.2
DDT	21.0	11.9
	30.0	0.6
	31.0	0.4
	37.0	0.2

In summary, free-radical catalysis has not shown as extensive degradation of DDT as some other systems. The peroxide catalyst examined has catalyzed decomposition only to DDE at 100°C, and was substantially unreactive at 50°C. The non-peroxide free-radical catalyst, azobis isobutyronitrile, was ineffective at both 50°C and 100°C, as was the inorganic peroxide salt potassium persulfate. However, the initial test with the ambient-temperature redox system shows some promise in that 88% of the DDT was destroyed with 27% being found in degradation products other than DDE.

Alkaline Hydrolysis

It is reported in the literature that the reaction of DDT with ethanolic KOH (ambient or reflux) yields DDE as a product, yet refluxing with alkaline-ethylene glycol gives di(p-chlorophenyl)acetic acid, DDA (Reference 27). A series of experiments were carried out to further establish the extent to which alkaline hydrolysis reactions would take place. In these tests, ethylene glycol, n-butanol, and ethanol were made 1 N in KOH and refluxed with DDT. Samples were withdrawn for analysis after 1, 2, 4, and 8 hours and subjected to gas chromatographic analysis. The reflux temperatures were respectively 168 to 175°C, 117°C, and 78° C.

The results when ethylene glycol is the solvent follow:

		Analysis, %, after Reaction, Hrs, at 168 to 175°C			
Component	Retention Time, Min	1	2	4	8
	6.6	(2.4)	(18.7)	(57.1)	(90.4)
	8.4	0.2	-	-	-
DBP	9.4	0.1	-	-	-
DDMU	13.4	0.1	0.8	-	-
DDE	15.6	32.2	21.8	2.7	0.5
DDT	21.0	-	-	-	-

These results show several interesting factors. The DDT has been completely consumed in all of the experiments and the DDE was gradually reacted so that it too was nearly consumed after 8 hour reaction. A new, unidentified peak with a retention time of 6.6 min was shown and the build-up of this peak was nearly proportional to the reaction time, after an approximately half-hour induction period. This peak cannot be quantitated until it is isolated and a calibration curve determined; the results shown are on the basis of the DDT calibration curve. The data are shown only to demonstrate that the peak builds up in a near-linear manner with increased reaction time. The balance of products shown by gas chromatographic analysis falls far short of 100%, 65% of the products after 1 hour reaction not being accounted for. This presumeably represents production of DDA, or a similar product which does not respond to the gas chromatograph.

Reduction of the reflux temperature to 117° by using n-butanol as the solvent yielded the following results:

Component	Retention Time, Min	Analysis,[b] %, after Reaction, Hrs, at 117°C in KOH-n-butanol			
		1	2	4	8
	1.8	0.3	0.3	0.2	0.2
	2.4	0.3	0.3	0.2	0.2
	3.6	0.3	0.3	0.2	0.5
	4.8	0.1	0.2	0.2	0.2
	7.0	0.3	0.2	0.2	0.2
	8.7	4.8	3.0	2.7	1.7
	11.7	1.3	2.7	3.1	2.7
	12.8	0.4	0.3	0.4	0.2
DDMU	13.5	1.0	1.1	1.2	0.5
DDE	15.6	63.9	57.3	47.0	41.1
	18.5	0.4	0.2	0.2	0.2
DDT	21.0	-	-	-	-
	23.1	<0.1	<0.2	<0.2	0.2
	24.0	12.8	10.8	23.5	25.0
	28.5	0.1	<0.2	0.2	0.2
	29.4	4.6	3.3	7.6	12.7
	36.0	<0.1	<0.2	<0.2	0.2
	37.3	<0.1	<0.2	<0.2	0.7
	38.2	<0.1	<0.2	<0.2	0.2
	39.7	<0.1	<0.2	<0.2	0.2

The DDT was consumed in all of the experiments and it appears that the DDE formed is being gradually removed. Unidentified products with retention times of 24.0 and 29.4 min appear to be increasing with continued reaction time. Many trace quantities products were also shown. The balance of products indicates that up to 20% of a material which does not give a gas chromatographic response was also present; this product may be DDA.

The results of a similar experiment in which DDT was refluxed with 1N KOH in ethanol can also be examined.

Component	Retention Time, Min	Analysis, %, after Reaction, Hrs, at 78°C in KOH-Ethanol			
		1	2	4	8
	8.0	0.2	0.6	0.4	0.2
	9.2	0.1	1.0	0.2	0.2
	11.3	3.0	6.4	2.5	2.2
DDMU	13.1	5.2	13.9	3.8	3.3
DDE	15.6	83.8	59.0	91.2	93.3
	16.8	0.4	3.2	0.2	-
DDD	17.8	2.9	15.3	1.7	1.2
	18.4	0.1	0.7	-	-
DDT	21.2	-	-	-	-

Although the results are scattered, the principal product is DDE, as expected, although minor or trace quantities of a variety of other products were obtained also.

In summary, it is clear that DDT may be simply dehydrochlorinated to the dichloroethylene derivative DDE but the further transformation of this species to a product expected to be harmless to the environment appears to require extremely drastic conditions. Alkaline hydrolysis appears to offer little promise as a practical means for degrading DDT to a product compatible with environmental requirements.

Oxidation

The oxidation of DDT is another means of destruction of this pesticide that deserves examination. Two general approaches have been considered. In one, an oxidation of the DDT molecule was attempted with an acid-CrO_3 system. In the second system, an alkaline oxidation was considered on the basis that the alkaline condition would dehydrochlorinate the DDT to DDE, and the ethylenic structure thus formed would be susceptible to oxidation, possibly to the soluble acetic acid derivative, DDA.

CrO_3-Acetic Acid

The oxidation of DDT and DDE by CrO_3-acetic acid was reported by Grummitt, Buck and Jenkins (Reference 28), who reported "no identified products" from DDT oxidation, and 4,4'-dichlorobenzophenone (DBP) as a product of DDE oxidation. In the experiment which was carried out, 2g of DDT were refluxed (117 to 120°C) in 50 ml of glacial acetic acid containing 1.6 g of CrO_3. A 10 ml sample was withdrawn after 1, 2, 4 and 8 hour reflux, with 10 ml of glacial acetic acid being added to the reflux mixture to maintain a constant volume. The mix turned a dark green color within one hour and it appears that the CrO_3 was consumed in this period. The analytical results follow:

	Retention	Analysis, %, after Reaction, Hr, at 117-120°C			
Component	Time, Min	1	2	4	8
	1.4	0.1	0.1	0.2	0.7
	2.5	1.8	1.3	1.6	1.5
DBP	10.3	0.4	0.3	0.3	0.1
	15.0	0.1	0.1	0.1	<0.1
DDE	15.8	6.9	4.7	6.9	4.6
	18.8	0.7	0.2	0.5	0.1
DDT	21.0	61.7	54.1	64.6	59.7
Material unaccounted for, %		28.3	39.2	25.8	33.3

Although the results show scatter, it is clear that at least half of the DDT was not consumed under the rigorous oxidation conditions employed. A substantial amount of material(26 to 39%) was unaccounted for in the gas chromatographic analysis. It is considered likely that the 26 to 39% of material not shown in the analyses represents products such as DDA or p-chlorobenzoic acid, neither of which will respond to conventional gas chromatography unless derivatives are formed. No attempt was made to further identify the products since a substantial amount of the DDT was unreacted under extremely rigorous oxidation conditions - conditions much more severe than might be used for a practical field destruction process of DDT degradation.

Alkaline $KMnO_4$

Attempts have been made to oxidize DDT with alkaline $KMnO_4$. In the initial experiment, 1 g of DDT was dissolved in 45 ml of acetone and 1 g of $KMnO_4$ and 5 ml 10 N aq. KOH were added. An immediate reaction leading to the production of a voluminous brown precipitate of MnO_2 was observed. However, analysis of the solution showed DDE as the only pesticide product and a blank reaction yielded a similar MnO_2 precipitate when the alkaline $KMnO_4$ was reacted with acetone.

Similar results were obtained when dioxan and tetrahydrofuran were examined as solvents for the reaction.

The reaction of DDT with $KMnO_4$ and pyridine was attempted also. The pyridine was refluxed with $KMnO_4$ to remove impurities, and then distilled before use. The experimental conditions were as follows:

a. 1 g DDE + 1 g $KMnO_4$ +10 ml pyridine reacted 67 hr at 25°C.

b. 1 g DDT + 1 g $KMnO_4$ + 10 ml pyridine reacted 69 hr at 25°C.

c. 1 g DDT + 1 g $KMnO_4$ + 1 ml 10 N KOH + 10 ml pyridine reacted 71 hr at 25°C.

The data for these experiments follows:

		Analysis, %		
Component	Retention Time, Min	(a)DDE, $KMnO_4$ pyr.	(b)DDT, $KMnO_4$ pyr.	(c)DDT, alk$KMnO_4$ pyr.
DBP	9.5	6.9	-	6.9
	12.2	-	<0.1	-
DDMU	13.1	-	1.3	-
DDE	15.6	96.4	8.6	79.0
DDD	18.1	-	0.2	-
DDT	21.0	-	80.3	-

The results indicate little hope for a successful oxidative degradation of DDT.

TOXICOLOGY OF DDT DEGRADATION PRODUCTS

With the development of bis(p-chlorophenyl) ethane as a probable product of the reductive degradation of DDT, information has been sought on the toxicology of this material.

Van Oettingen (Reference 29) states that "2,2-bis(p-chlorophenyl) ethane is void of the neurotoxic effects of DDT." The LD_{50} for rats (oral administration) was 1000 mg/kg (Reference 30). Comparative acute toxicity values (LD_{50}) were 150 mg/kg for DDT.

SECTION V

DEGRADATION OF DDT BY METALS

The initial promise that was shown by the DDT degradation technique of mildly acidic reduction by zinc powder led to a more complete examination of this reaction, as well as tests with other materials having similar reducing power.

DDT DEGRADATION BY ZINC

A series of tests were carried out in an effort to characterize the zinc reduction and determine means for improving the reaction. The basic test involved the solution of 1 g of DDT in 20 ml acetone, the addition of 1 g of zinc powder, and acidification with 10 ml of 10% acetic acid, giving a final acidity of 0.5 N.

Rate of Zinc-Acetic Acid Reduction of DDT

An experiment was carried out to determine the effect of time on the reaction. Time intervals from 1/4 hour to 27 hours at 25°C were employed. The analytical results follow:

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 25°C				
		1/4	1	2	3	27
	3.1	0.1	-	-	-	-
	6.6	1.1	1.0	1.0	0.8	1.2
DDEt	7.8	20.0	18.5	20.3	24.5	20.0
	9.8	1.4	0.8	0.8	0.8	0.7
	11.8	0.1	0.1	0.1	0.1	0.1
	12.4	0.1	0.1	0.2	0.4	0.2
DDMU	13.0	18.8	13.6	15.5	20.0	16.2
DDMS	14.2	7.9	7.5	9.8	10.0	16.8
DDE	15.6	11.2	5.9	2.5	2.3	-
DDD	18.0	16.2	23.2	21.0	19.9	17.3
DDT	21.0	7.7	6.5	2.1	1.4	-

These results show that substantially all of the DDT has been reduced within the first 15 min, and that the small amount of DDE which appears in the initial sample is soon consumed; DDD is formed early in the reaction but tends to be reduced to DDMS.

Tests were made in which reaction times as long as 28 days were investigated. In each case the reaction of 1 g of DDT with 1 g of technical grade zinc dust in the dilute acetic acid-acetone medium was used.

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 25°C						
		24	48	97	170	340	504	673
	7.0	0.2	0.5	0.4	<0.2	0.2	-	0.3
DDEt	7.8	30.2	28.1	31.4	33.8	35.7	35.6	38.2
	10.2	-	-	-	-	-	-	0.5
	12.0	<0.2	<0.2	0.2	<0.2	<0.2	-	0.1
	12.4	-	-	-	-	-	0.2	0.3
DDMU	13.0	5.7	6.7	5.5	4.7	5.4	4.9	4.1
DDMS	14.0	21.2	28.8	35.1	37.3	41.8	46.7	43.4
DDD	17.8	42.5	36.0	27.3	24.0	16.4	12.5	13.0
DDT	21.0	-	-	-	-	-	-	-

These results show that the DDD that appears to be formed in the early stages of the reaction is slowly consumed during continued reaction, with an equivalent buildup of the concentration of DDEt, the monochloroethane derivative of DDT, DDMS, and possibly 4,4'-dichlorostilbene (which occurs at approximately the same place in the gas chromatogram). A small amount of material with a 13 min gas chromatographic retention time which appears to be slowly consumed is shown also; this material is probably the chloroethylene derivative, DDMU.

Effect of Increased Temperature on Zinc-Acetic Acid Reduction of DDT

The effect of increased temperature on the rate of reaction was of interest, since a slight increase in temperature may yield somewhat increased reduction of the DDT. A series of tests in which the extent of reaction was to be measured after 1, 4, 7, 14, 21 and 28 days at 40°C was therefore initiated. This temperature was chosen as a conservative simulation of summertime soil conditions in Southern U.S. fields; Bowman, Schechter and Carter used a 45°C temperature in persistence tests as the highest temperature to which Georgia soils were likely to be subjected (Ref. 34). In these tests 1 g of DDT was reacted with 1 g of zinc dust in 10 ml of 10% acetic acid and 20 ml of acetone. The results follow:

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 40°C						
		24	48	96	168	333	502	673
	7.0	0.2	0.2	0.3	0.7	0.9	0.3	0.3
DDEt	7.8	31.1	36.0	38.3	37.5	37.5	39.3	39.6
	10.5	0.4	0.3	-	0.3	0.4	0.5	0.6
	12.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	12.4	0.5	0.1	-	0.4	0.5	0.7	0.9
DDMU	13.0	5.1	5.1	4.6	4.9	5.1	4.5	5.3
DDMS	14.0	40.6	51.4	55.8	55.8	55.5	54.5	53.0
DDD	17.8	22.0	6.9	0.8	0.3	-	0.2	0.1
DDT	21.0	-	-	-	-	-	-	-

The major effect of higher reaction temperature appears to be the more rapid and complete reduction of DDD to DDMS.

Effect of Concentration of Zinc on DDT Reduction

The screening tests have used 1 g of zinc to reduce 1 g of DDT. It was of interest to vary the ratio of zinc to DDT and determine the effect on the reaction. Tests have subsequently been made in which 1 g, 0.5 g, 0.25 g and 0.1 g of CP zinc dust were reacted with 1 g of DDT in the dilute acetic acid-acetone medium; the materials were reacted for 2 days at 25°C.

The normal appearance of the reaction is that a voluminous precipitate of DDT appears immediately upon mixing, but that the precipitate disappears after about 15 min reaction, when the DDT appears to have been essentially consumed. In this test, samples with 1g and 0.5 g Zn led to dissolution of the DDT after 15 min mixing, and the sample containing 0.25 g Zn resulted in nearly complete solution of the DDT in 15 min and complete solution in 24 hr. The sample with 0.1 g of Zn did not appear to yield complete solution of the DDT. The analyses of these samples follow:

Component	Retention Time, min	Analyses, %, after 48 hr Reaction at 25°C			
		g Zinc dust reductant/g DDT			
		1.00	0.50	0.25	0.10
DDEt	7.8	35.1	28.5	13.5	6.8
	11.0	0.1	0.2	0.3	-
	12.0	0.3	0.2	0.1	0.2
DDMU	13.0	4.4	4.3	2.4	1.3
DDMS	14.0	20.6	15.2	5.6	1.6
DDE	15.6	-	-	1.7	3.8
DDD	17.8	39.4	51.7	46.7	18.4
DDT	21.0	-	-	29.8	67.8

These results show clearly that a reduced amount of zinc results in a less complete reduction of the DDT. Indeed, the equal weight ratio resulted in the highest concentration of DDEt product, as well as a somewhat reduced amount of DDD and an increased concentration of DDMS and/or 4,4'-dichlorostilbene. An examination of the stoichiometry of the reaction of DDT and zinc reveals that 0.276 g of zinc would be consumed in reducing 1 g of DDT to the product DDEt. However, these results suggest that an excess of zinc may be required for effective reaction. It should be noted that unconsumed zinc was found in all samples - including the one in which 0.1 g of zinc was used per g of DDT.

A test was also carried out in which 0.1 g of granular CP zinc was used per gram of DDT. The results were in reasonable agreement with those tabulated above, with 72.6% of the DDT remaining, 10.1% being present as DDD and 11.8% as DDEt.

Effect of Acidity on Zinc Reduction of DDT

The screening tests have shown that DDT may be reduced by zinc in the presence of either 10% acetic acid, or $(NH_4)_2SO_4$ with 95% ethanol. The former reaction has generally been studied at 25° while the latter tests (Romano reaction) were generally carried out at reflux temperature (78°C). Accordingly, tests were carried out to determine the effect of acidity on the extent of DDT reduction by zinc, in an effort to establish suitable reaction conditions.

In the first series of tests, the zinc-acetic acid-acetone system was examined. In each test, 1 g of DDT, 1 g of zinc dust, and 20 ml acetone were reacted with 10 ml of aqueous acetic acid of varying strength. The results are given in terms of the acidity of the final reaction mixture; the reactions were all carried out for 96 hrs at 25°C. The analyses follow:

Com-	Retention	Analysis, %, after Reaction for 96 hrs at 25°C as a Function of Acetic Acid Normality of Reaction Mixture				
ponent	Time, min	5 N	1 N	.25 N	.05 N	.005 N
	4.0	-	-	0.1	0.1	0.1
	6.8	-	0.2	0.1	0.3	0.2
DDEt	7.8	63.2	32.5	31.1	32.1	45.9
	10.2	0.1	0.1	0.4	0.1	-
	12.0	0.1	0.1	0.1	0.1	0.1
DDMU	12.8	2.7	4.6	7.6	8.3	3.5
DDMS	14.0	15.6	37.3	31.8	20.7	14.7
DDD	17.8	14.0	24.9	28.5	38.3	35.6
DDT	21.0	-	-	-	-	-

These results show the greatest conversion of DDT to the ethane derivative, DDEt, at the extremes of acidity employed. It is particularly noteworthy that the extensive conversion of DDT to DDEt achieved with the 5 N acidity also showed minimal DDD and presumably the monochloroethane derivative, DDMS. The low-acidity extreme also showed a high conversion of DDT to DDEt, but the residual DDD was also high; the visual appearance and slow solubility of the flocculent precipitate on the initiation of the reaction also indicated a slower reaction with the 0.005 N sample. However, both extremes appeared to give a more extensive reaction than samples more nearly equivalent to the 0.5 N medium normally employed.

A sample was also examined in which the medium was 0.5 N in acetic acid but to which 0.2 g of the surface active agent Triton X-100 was added. The surfactant appeared to have no substantial effect on the reaction.

Component	Retention Time, min	Analysis, %, after Reaction for 96 hrs at 25°C
	6.8	0.2
DDEt	7.8	32.7
	10.2	0.3
	12.0	0.1
	12.4	0.1
DDMU	12.8	6.1
DDMS	14.0	36.6
DDD	17.8	23.9
DDT	21.0	-

In view of the suggested possibility that the reduction of DDT in the field might be carried out using acidity developed by soil sulfur (Section IX), tests were carried out in which the acidity for the reaction was provided by sulfuric and sulfurous acids. The test with sulfuric acid was conducted using 10 ml of 1.5 N H_2SO_4 in place of the 1.5 N acetic acid normally employed. The sulfurous acid was prepared by bubbling SO_2 into water; the solution assayed 2.0 N in sulfurous acid. The results of the analyses follow; the acidity indicated is that of the final reaction mix:

Component	Retention Time, min	Analysis, %, after Reaction for 24 hr at 25°C	
		0.5N in H_2SO_4	0.7N in H_2SO_3
DDEt	7.8	39.4	12.2
	12.0	0.3	0.2
DDMU	13.0	4.9	3.4
DDMS	14.0	14.2	-
	14.8	-	1.0
DDE	15.6	-	4.1
DDD	17.8	41.2	45.6
DDT	21.0	-	33.3

These results indicate substantially greater reaction in the presence of sulfuric acid. The reaction in the presence of the H_2SO_4 or an equivalent amount of acetic acid appears approximately the same.

The reduction of DDT by zinc has been achieved in a medium of refluxing 95% ethanol in which the acidity was supplied by the slightly acid salt $(NH_4)_2SO_4$. A series of tests were carried out in which this reaction was examined at 25° (rather than the reflux temperature of 78°C) and in which the salts $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl were compared. In these tests, 1 g of DDT and 1 g of zinc powder were reacted with 2 g of the ammonium salt in 50 ml of 95% ethanol. The samples were allowed to settle and probe samples (1 microliter) were withdrawn for analysis periodically. The results of the tests with $(NH_4)_2SO_4$ were as follows:

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 25°C			
		71	144	334	593
DDEt	7.8	1.2	5.2	6.2	6.1
	12.0	0.2	-	-	-
DDMU	13.0	0.4	0.5	1.4	4.6
	14.5	0.2	0.1	0.3	0.2
DDE	15.6	10.7	6.5	10.8	5.5
DDD	17.8	2.3	6.6	7.2	6.4
DDT	21.0	84.9	81.1	74.1	77.2

When the salt NH_4NO_3 was used, the results were as follows:

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 25°C			
		75	172	334	526
DDEt	7.8	0.8	1.1	1.0	0.9
	10.5	-	0.1	0.4	0.7
	12.0	-	0.1	-	-
DDMU	13.0	1.1	2.8	1.7	0.3
DDMS	14.0	-	-	0.1	0.2
	14.4	-	-	-	0.1
DDE	15.6	3.0	1.8	4.0	0.7
	16.0	-	-	-	0.1
DDD	17.8	10.4	12.3	13.4	14.0
DDT	21.0	84.6	81.8	79.4	82.6

The results with the salt NH_4Cl follow:

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 25°C			
		75	172	334	527
	4.0	-	-	-	0.1
DDEt	7.8	25.3	34.8	32.5	34.4
	10.0	0.4	0.4	0.6	0.6
	12.0	0.1	0.1	0.1	0.1
	12.5	-	-	0.1	0.1
DDMU	13.0	2.1	1.6	1.8	1.8
DDMS	14.0	7.7	8.4	8.8	8.6
DDE	15.6	0.3	0.1	0.1	0.2
	16.0	0.7	0.6	0.7	0.5
DDD	17.8	52.1	47.6	49.8	48.2
DDT	21.0	11.4	6.4	5.5	5.6

These results show a substantial 25° degradation of DDT when the acidity is provided by NH_4Cl, although the reaction is not nearly as rapid as that observed at ambient temperature in the presence of dilute acetic or sulfuric acids. Reduction in the presence of $(NH_4)_2SO_4$ and NH_4NO_3 is much slower and does not appear to proceed to a useful extent of reaction.

In a further test of the effect of the pH of the reaction mix on the extent of reaction, a test was conducted with a basic medium. In this test 1 g of DDT was reacted with 1 g zinc dust in 20 ml acetone plus 10 ml of water containing 1 g of sodium hydroxide (reaction mix 0.8 N in NaOH). The results follow:

Component	Retention Time, min	Analysis, %, after Reaction for 72 hr at 25°C
DDEt	7.8	4.9
DDMU	13.0	71.6
DDE	15.6	23.5
DDD	17.8	-
DDT	21.0	-

The basic reaction was interesting in that the DDT was entirely consumed without forming DDD. A quantity of DDE was observed, as might be expected in a basic reaction, but the major product (72%) appears to be DDMU, the monochloroethylene derivative of DDT. About 5% of the DDEt was also observed.

Effect of Particle Size and Quality of Zinc

The effect of both the particle size of zinc and the quality of the material was investigated in some tests in which the efficacy of DDT reduction was compared using technical grade and CP grade dust, and CP grade granular material. In each test, 1 g of DDT was reacted with 1 g of zinc, 10 ml of 10% acetic acid and 20 ml of acetone. The results follow:

		Analysis, % after 46 hr Reaction at 25°C			
	Zinc Product:	CP granular	CP granular	CP dust	Tech. dust
Component	Retention Time, min				
DDEt	7.8	45.0	41.6	35.1	31.1
	11.0	-	0.1	0.1	-
	12.0	0.1	0.1	0.3	0.2
DDMU	13.0	2.7	2.6	4.4	4.4
DDMS	14.0	5.5	5.6	20.6	37.2
DDE	15.6	0.5	0.4	-	-
DDD	17.8	45.0	45.3	39.4	27.1
DDT	21.0	1.2	4.4	-	-

No highly significant trends were shown by these tests. Although the granular zinc produced the largest amount of the DDEt product, this material also yields an undesirably large amount of DDD as a product. The largest amount of material with a 14 min gas chromatographic retention time (presumably DDMS and 4, 4'-dichlorostilbene) was produced by the zinc dust reductant, and indeed the technical grade dust was more efficient in producing this product than the CP grade zinc dust.

Zn Reduction of Technical DDT

Although substantial reduction of pure p, p' -DDT has been shown by Zn in the dilute acetic acid-acetone solvent system, it remained to be established that similar results would be obtained with commercial-grade DDT. Three samples were examined and in each case, complete destruction of the p, p'-DDT was shown, with a major amount of material being the bis(p-chlorophenyl) ethane. Another major peak appears to be p, p'-DDD with possibly some o, p'-DDT (an important impurity in technical DDT); additional analyses would be required to differentiate between these two materials which elute from the chromatographic column at essentially the same time. However, it is believed the peak probably represents p, p'-DDD since it is present in larger quantities than the o, p'-DDT in commercial DDT (generally ~20% o, p'-DDT).

		Analysis, %, after Reaction for 24 hr at 25°C		
	DDT Source:	Montrose Chemical	Diamond Shamrock	Eastman Organic Chems.
Component	Retention Time, min			
	1.3	<0.1	<0.1	0.9
	1.6	<0.1	<0.1	1.1
(1, 1-diphenylethane)	2.0	<0.1	-	-
	5.9	<0.1	<0.1	-
o, p'-DDEt (?)	6.6	6.0	7.1	5.2
p, p'-DDET	7.6	26.2	23.5	34.4
	11.3	<0.1	0.7	-
	12.4	1.3	3.1	1.3
DDMU	13.1	4.2	4.2	3.1
DDMS	14.2	12.0	12.5	7.4
p, p'-DDE	15.6	11.0	11.3	8.7
p, p'-DDD + o, p'-DDT	17.9	29.3	37.7	38.0
p, p'-DDT	21.0	0.1	-	-

Reduction of Commercial DDT Emulsion

Tests were made to determine the effect of the additives used in commercial spray formulations on the reduction of DDT by mildly acid zinc. In the initial test, the reduction of a 25% emulsifiable concentrate of DDT[*], to which an equivalent weight of heavy mineral oil had been added[**], was attempted. This formulation was chosen as a simulant of spray formulations. In the first test, 4 g of the 25% DDT emulsion and 4 g of the mineral oil were reacted with 1 g of zinc dust and 10 ml of 10% acetic acid. The reaction was carried out for 24 hr at 25°C. The results of the analysis of this sample indicated partial reduction of the DDT. Visual observation of the reaction indicated the DDT was held in the oil phase and appeared not to be effectively contacted by the zinc-aqueous acetic acid. A modification of the system to allow more effective mixing of the reactants was expected to provide essentially complete reaction. The analysis of the reaction products follows:

Component	Retention Time, min	Analysis, %, after 24 hr at 25°C
o,p'-DDEt - ?	6.8	2.9
p,p'-DDEt	7.8	10.8
	12.4	0.1
DDMU	13.0	0.5
DDMS	14.0	0.7
p,p'-DDE	15.6	4.4
p,p'-DDD + o,p'-DDT	17.8	17.6
p,p'-DDT	21.0	63.1

Additional tests are described in Section VIII of this report covering the reduction of DDT in water.

METAL REDUCTANTS OTHER THAN ZINC

Additional experiments were performed in which metals with similar electronegativity were substituted for zinc in the reduction of DDT. These tests were made with the 10% acetic acid-acetone solvent system as described earlier in the studies with zinc.

For comparison, reduced iron powder and aluminum flake and powder samples were employed. The results of the analyses show less reduction than was obtained with zinc under similar conditions. Data from a zinc reduction experiment are repeated for reference.

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[*]

DDT (setting point 89°C		25.0%
Xylene		55.1
Deodorized Kerosene		16.8
Emulsifiers:	Emnon 6932	2.0
	Agrimul 70A	1.0
Stabilizer:	Epichlorhydrin	0.1
		100.0%

[**] Nujol, extra heavy grade.

Experiments were also carried out using copper powder in place of zinc in the dilute acetic acid-acetone medium. Although a blue coloration of copper ion appeared in the reaction mix, the analytical data shows that no significant reduction of the DDT was achieved.

Component	Retention Time, min	Analysis, %, after 24 hr Reaction at 25°C
DDMS	13.8	0.3
DDE	15.5	5.0
DDT	20.8	94.7

Na_2SO_3, NaI, $CrCl_3$, $Na_2S_2O_3$ as Reductants

The inorganic reductants Na_2SO_3, NaI, $CrCl_3$ and $Na_2S_2O_3$ were also examined as reductants in place of zinc. In each case, the reaction was run in the 10% acetic acid-acetone medium used previously. The results with each of these reductants show that 55 to 90% of the DDT was not reduced, and that the major product was DDE (10-40%). None of these reductants produced the peak with an 8-min elution time, as was shown with the zinc reduction.

		Analysis, %, after Reaction for 118 hr at 25°C			
	Reductant:	Na_2SO_3	NaI	$CrCl_3$	$Na_2S_2O_3$
Component	Retention Time, Min				
	3.1	0.2	0.2	1.8	<0.1
DDMU	13.4	0.6	0.8	0.5	1.8
DDE	15.6	39.2	39.8	33.2	9.2
DDD	18.1	0.3	1.0	0.5	0.2
DDT	21.2	52.0	55.0	66.4	79.2

ZnS_2O_4, $Na_2S_2O_4$ as Reductants

The hydrosulfites are important commercial reducing agents which were investigated for their efficacy in reducing DDT. Both the zinc and sodium salts were tried. The solvent in each case was 95% ethanol. The $Na_2S_2O_4$ was also examined in a basic medium 1N in KOH. The results in each case showed little reduction of the DDT, with DDE being present as the most significant product. The $Na_2S_2O_4$-KOH reaction led to essentially complete conversion to DDE.

	Reductant:	Analysis, %, after Reaction for 48 hr at 25°C		
Component	Retention Time, min	ZnS_2O_4	$Na_2S_2O_4$	$Na_2S_2O_4$+KOH
	12.7	-	-	0.1
DDMU	13.6	-	-	0.8
	14.2	0.2	0.2	-
DDE	15.6	10.3	9.5	99.2
	19.0	0.1	0.3	-
DDT	21.4	89.4	89.3	-

Another test was made with sodium hydrosulfite in an aqueous acetone medium. A solution of 1 g of DDT in 20 ml acetone was added to 7 g of $Na_2S_2O_4$ dissolved in 20 ml of water and reacted for 2 hours at 25°C. The analytical data indicate approximately one-half of the DDT was converted to DDE, but no significant quantities of other products were found.

	Reaction, 2 hours at 25°C	
Component	Retention Time, min	%
	7.5	0.1
	8.4	0.1
DDMU	13.4	1.7
DDE	15.6	54.6
DDD	18.2	0.6
DDT	21.0	43.0

Na_2S as a DDT Reductant

Sodium sulfide was also examined as a DDT reductant. When the reaction was carried out in ethanol for 48 hr at 25°C, analysis showed only DDE as a product, the simple dehydrohalogenation in the basic medium being carried to completion with no reduction being observed.

Component	Retention Time, min	Analysis, % after Reaction for 48 hr at 25°C
DDE	15.6	98.5

$LiBH_4$ as a DDT Reductant

The hydrides represent a class of important reductants which deserve consideration. Since most of the simple metallic hydrides are insoluble in solvents for DDT, $LiBH_4$ was used in tetrahydrofuran solution.

The THF was dried over $LiBH_4$ before use. The results indicate little reduction of the DDT.

Component	Retention Time, min	Analysis, %, after Reaction for 3 hr at 25°C
(1, 1-diphenylethane)	1.8	1.0
DDMU	13.3	0.5
	14.5	0.2
DDE	15.3	5.0
DDD	17.7	7.6
DDT	20.8	85.9

MECHANICS OF REDUCTIVE DEGRADATION

Results reported in preceding sections have shown that zinc dust in weakly acid medium (10% acetic acid or $(NH_4)_2 SO_4$) led to the complete or nearly complete reduction of DDT, without forming DDE as a product. However, a series of other reductants with similar reducing potentials did not yield the essentially complete destruction of DDT shown by zinc. Therefore, further tests were made in an effort to better define the role of zinc in the reaction. Reactions were carried out in which the reductant was (a) magnesium, with a slightly greater reducing potential than zinc, (b) magnesium + zinc, (c) magnesium + $ZnCl_2$, (d) zinc in granular form, and (e) zinc in fine powder form. These tests were run with the 10% acetic acid-acetone solvent system as described earlier. One gm of DDT was reacted with the given amount of reductant (nominally 1 gm) in these tests. The reaction was carried out for one day at 25°C. The results of the analyses of the products follows:

	Reductant:	Analysis, %				
Component	Retention Time, min	Mg 1.00 gm	Mg 0.90 gm Zn gran. 0.10 gm	Mg 1.00 gm $ZnCl_2$ 0.164 gm	Zn gran. 1.00 gm	Zn powder 1.00 gm
DDEt	8.0	-	0.3	8.7	50.7	31.2
	12.0	-	-	-	-	0.1
DDMU	13.1	0.4	1.2	0.7	4.1	6.0
DDMS	14.0	0.1	0.4	1.7	4.6	18.0
DDE	15.5	10.7	8.3	5.9	0.5	-
DDD	18.0	4.0	15.3	26.4	38.4	44.8
DDT	21.0	84.8	74.4	56.7	1.7	-

These result show that the reduction of DDT by magnesium proceeds to some degree when a small amount of $ZnCl_2$ is present, or to a lesser extent when zinc metal is used with the Mg. However, in neither case was the reaction as efficient as that obtained with zinc metal alone as the reductant. The reaction with 20 mesh zinc granules appeared to progress slightly better than that with zinc powder in this test.

Additional tests were made in which $ZnCl_2$ was used in conjunction with aluminum, iron, NaI and Na_2SO_3 - systems that showed a small reduction of DDT in earlier tests. In the experiments with aluminum, fresh samples of aluminum granules and aluminum powder were used as the reductant. The experiments were carried out using the metal as the reductant, and adding zinc ion in order to observe any specific effect of the zinc. The results of the analyses from the tests with aluminum follow:

		Analysis, %, after 46 hr Reaction at 25°C			
	Reductant:	Al granules (1 g)	Al granules (1 g) $ZnCl_2$ (.164 g)	Al powder (1 g)	Al powder (1 g) $ZnCl_2$ (.165 g)
Component	Retention Time, min				
	12.0	0.1	0.1	0.1	0.1
	13.0	1.7	1.0	3.0	1.8
DDE	15.6	2.2	1.8	2.8	3.6
DDD	17.8	0.4	0.4	0.7	2.2
DDT	21.0	95.5	96.9	92.6	92.3

These results show that the aluminum was ineffective in reducing DDT, both as the powder and in granular form. Added zinc ion had no significant effect on the reduction.

The reductants sodium iodide and sodium sulfite with added zinc ion were also examined but showed no significant effect in reducing DDT to a desirable end product. In these tests, 1 g of the DDT with 1 g of the reductant salt and 0.16-0.17 g of $ZnCl_2$ were reacted in the medium composed of 20 ml acetone and 10 ml of 10% acetic acid. The results of the analyses are as follows:

		Analysis, %, after 46 hr Reaction at 25°C	
	Reductant:	NaI (1 g) $ZnCl_2$ (.165 g)	Na_2SO_3 (1 g) $ZnCl_2$ (.173 g)
Component	Retention Time, min		
DDMS	14.0	0.2	0.2
DDE	15.6	7.2	5.1
DDD	17.8	0.7	0.5
DDT	21.0	91.9	94.2

Results reported earlier showed that some reduction of DDT was obtained when iron was used as the reductant, although the extent of reaction was significantly less than that obtained with zinc. A further test was carried out in which some zinc ion (as $ZnCl_2$) was added to the reaction mix in an effort to increase the reactivity. In this test 1 g of DDT was reacted with 1 g of iron powder + 0.164 g of $ZnCl_2$; the usual dilute acetic acid-acetone solvent mixture was employed. The following results were obtained:

Components	Retention Time, min	Analysis, %, after 24 hr Reaction at 25°C
DDEt	7.8	1.5
DDMS	14.0	0.7
DDE	15.6	4.9
DDD	17.8	17.4
DDT	21.0	75.6

The possibility that an easily consumed impurity, such as ZnO, may promote the reaction, or that impurity metals could catalyze the reduction of DDT was considered. In one series of experiments, finely powdered zinc oxide was added to the reaction mix in an effort to establish the effect on the extent of reaction. In this test, zinc oxide was added to the usual reaction mix of 1 g of DDT, 1 g of zinc dust, 10 ml of 10% acetic acid and 20 ml acetone. The reaction was carried out for 90 hr at 25°C. The results were as follows:

Component	Retention Time, min	Analysis, %, after 90 hr Reaction at 25°C			
		1.00 g Zn	+0.01 g ZnO	+0.1 g ZnO	+1 g ZnO
	6.8	0.2	0.1	0.2	0.1
DDEt	7.8	32.5	34.2	30.8	25.9
	10.0	0.1	0.4	0.5	0.5
	12.0	0.1	0.1	0.1	-
	12.4	-	0.4	0.5	0.2
DDMU	13.0	4.6	5.1	5.1	4.8
DDMS	14.0	37.6	39.3	41.5	30.6
DDD	17.8	24.9	20.1	21.5	37.8
DDT	21.0	-	-	-	-

Clearly, the added zinc oxide has not promoted a more extensive degradation of the DDT; indeed, the results with increasing zinc oxide suggest a reduced degradation of the DDT. The loss of reduction with increased zinc oxide may represent the consumption of acid by the basic oxide.

SECTION VI

DEGRADATION OF DDT BY CATALYZED METALS

CATALYZED ZINC REACTIONS

Reduction of DDT Using Zinc-Copper Couple

The studies described previously have shown that zinc dust in weakly acid medium leads to complete or nearly complete reduction of DDT. However, on close examination of the data, it appears that a complex two-path reaction may be involved. A portion of the DDT appears to be converted rapidly to the ethane derivative, DDEt, losing all three aliphatic chlorine atoms. Another portion appears to be reduced by the route DDT⟶DDD⟶DDMS⟶DDEt; the stepwise dechlorination involved in the second pathway appears to be a slower process. It was important, therefore, to determine the conditions that promote the apparently rapid and more complete reduction of DDT to bis(p-chlorophenyl)ethane (DDEt).

The possibility that metallic impurities in the zinc may act as catalysts was considered. In one test a milli-mole of copper ion was added to form a zinc-copper couple. Zinc-copper couples are used to advantage in some organic reductions (Reference 35). Other reaction conditions were the same as previously employed (1 g DDT, 1 g zinc dust, 10 ml 10% acetic acid, 20 ml acetone). The reaction was carried out for 90 hr at 25°C. The analysis of the products follows:

Component	Retention Time, min	Analysis, %, after 90 hr Reaction at 25°C
	4.0	0.1
	6.8	1.2
DDEt	7.8	85.0
	10.0	0.1
	12.0	0.1
DDMU	13.0	3.5
DDMS	14.0	10.1
DDE	15.6	-
DDD	17.8	-
DDT	21.0	-

This test was significant in that almost complete conversion to the ethane derivative of DDT, DDEt, was obtained. It should also be noted that no DDT, DDD or DDE was shown by the analysis. Additional tests with the metal couple were performed in order to further define the role of this important additive.

Tests were carried out in which the rate of the reduction of DDT by the zinc-copper couple was compared with that of zinc reduction, and in which the ratio of zinc-to-copper was varied.

In one series of tests, the couple was formed by adding the aqueous copper solution (1 meq of $CuCl_2$) to the acetone solution of DDT (1 g DDT in 20 ml acetone) in which the zinc (1 g) was suspended. The copper appeared to precipitate on the zinc surface, leading to the formation of a very dark (brown to black) precipitate, rather than the usual grey of the zinc. After the formation of the couple, 10 ml of 10% acetic acid was added; the final solution was then 0.5 normal in acetic acid (technical-grade zinc dust was used in these tests). The results of assay at a series of times follows:

Component	Retention Time, min	Analysis, %, after reaction, hrs, at 25°C				
		1/4	1	2	4	8
	6.8	0.9	1.7	1.2	4.3	1.5
DDEt	7.8	56.7	54.5	62.4	68.7	72.5
	10.6	0.1	0.4	0.4	0.1	0.3
	11.9	0.1	0.1	0.4	0.1	0.1
DDMU	12.8	3.2	4.0	4.0	3.4	5.0
DDMS	14.0	4.4	7.4	8.0	7.9	11.2
DDE	15.6	0.2	0.1	0.1	0.1	0.1
DDD	17.8	34.4	31.8	23.5	15.4	9.2
DDT	21.0	-	-	-	-	0.1

These results show a larger portion of the DDEt is formed within the first 15 min, and that most of the DDD produced initially is consumed in 8 hr at ambient temperatures.

In another series of tests, the copper (1 meq) was added after the acid (the reaction appears to be initiated on acid addition). The results of these tests are as follows:

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 25°C		
		1/4	2	4
	6.8	0.1	0.1	0.2
DDEt	7.8	47.4	63.1	66.5
	10.6	0.1	0.1	0.1
	11.9	0.1	0.1	0.1
DDMU	12.8	4.9	3.8	3.5
DDMS	14.0	4.7	7.5	9.8
DDE	15.6	0.2	<0.1	<0.1
DDD	17.8	42.3	25.2	19.5
DDT	21.0	0.1	-	0.1

These results are in reasonable agreement with the previous series, indicating that the order of copper addition does not appear to be a large factor in the reaction.

A comparative series of tests in which the zinc powder (technical-grade dust) was used as the reductant without the added copper, gave the following results:

Component	Retention Time, min	Analysis, %, after Reaction, hrs, at 25°C				
		1/4	1	2	4	8
	6.8	-	0.2	0.1	0.1	0.1
DDEt	7.8	24.6	28.7	27.7	26.9	26.5
	10.6	0.3	0.5	0.4	0.1	0.2
	11.9	0.1	0.2	0.1	0.1	0.1
	12.4	-	0.4	0.2	-	0.2
DDMU	12.8	5.5	5.1	5.6	5.7	5.9
DDMS	14.0	12.4	13.7	15.5	21.7	23.9
DDE	15.6	-	-	-	-	-
DDD	17.8	56.5	51.1	50.4	45.3	43.0
DDT	21.0	0.7	-	-	-	-

A comparison of the results obtained with the zinc-copper couple, and those using zinc alone as the reductant, reveal a dramatic difference. The amount of DDEt product formed in an equivalent time was 1.9 to 2.7 times greater in the samples in which the zinc-copper couple was used, compared to those in which zinc was the reductant. The samples using the zinc-copper reductant also produced less DDD as a product; the ratio of DDD when zinc was used for reducing compared to the zinc-copper samples ranged from 1.6 after 15 min to 4.7 after 8 hrs. The amount of the monochloroethane intermediate, DDMS, was also less when the zinc-copper couple was employed by a factor of 1.8 to 2.8. A comparison of the results is shown graphically in Figures 1, 2 and 3 following.

In an additional set of samples, the extent of reaction after 15 min at 25°C was determined, using CP grade zinc powder rather than the technical grade product used in the above studies. In this set of experiments a comparison was made between samples of DDT reduced with zinc, and with the zinc-copper couple. The results follow:

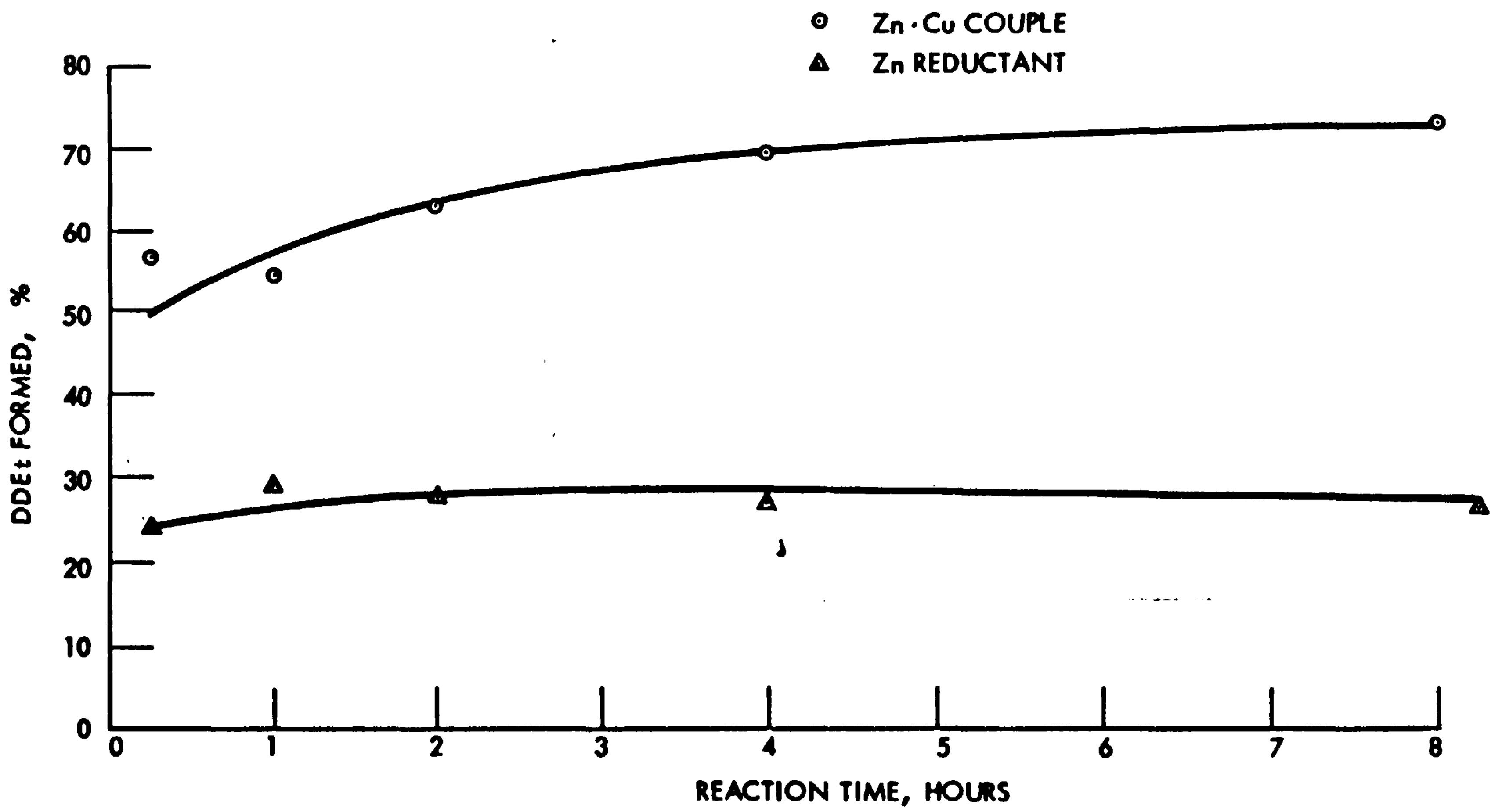

Figure 1

Rate of Formation of bis(p-Chlorophenyl) Ethane Product (DDEt) at 25°C When DDT Reduced with Zn·Cu Couple, or Zn Powder

Solution 0.5 N in Acetic Acid

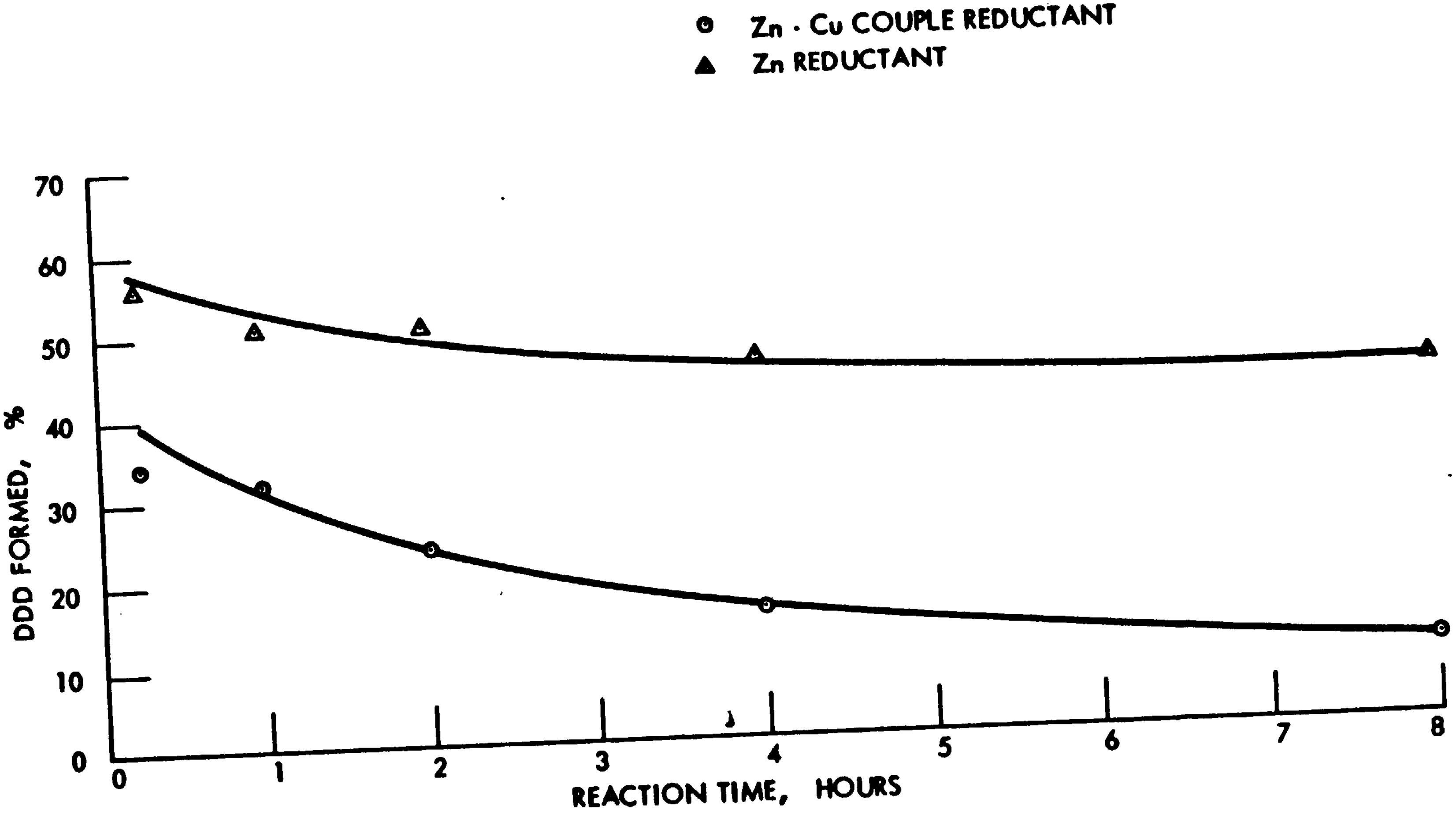

Figure 2

Rate of Formation of bis(p-Chlorophenyl) Dichloroethane Product (DDD) at 25°C When DDT Reduced with Zn·Cu Couple, or Zn Powder

Solution 0.5 N in Acetic Acid

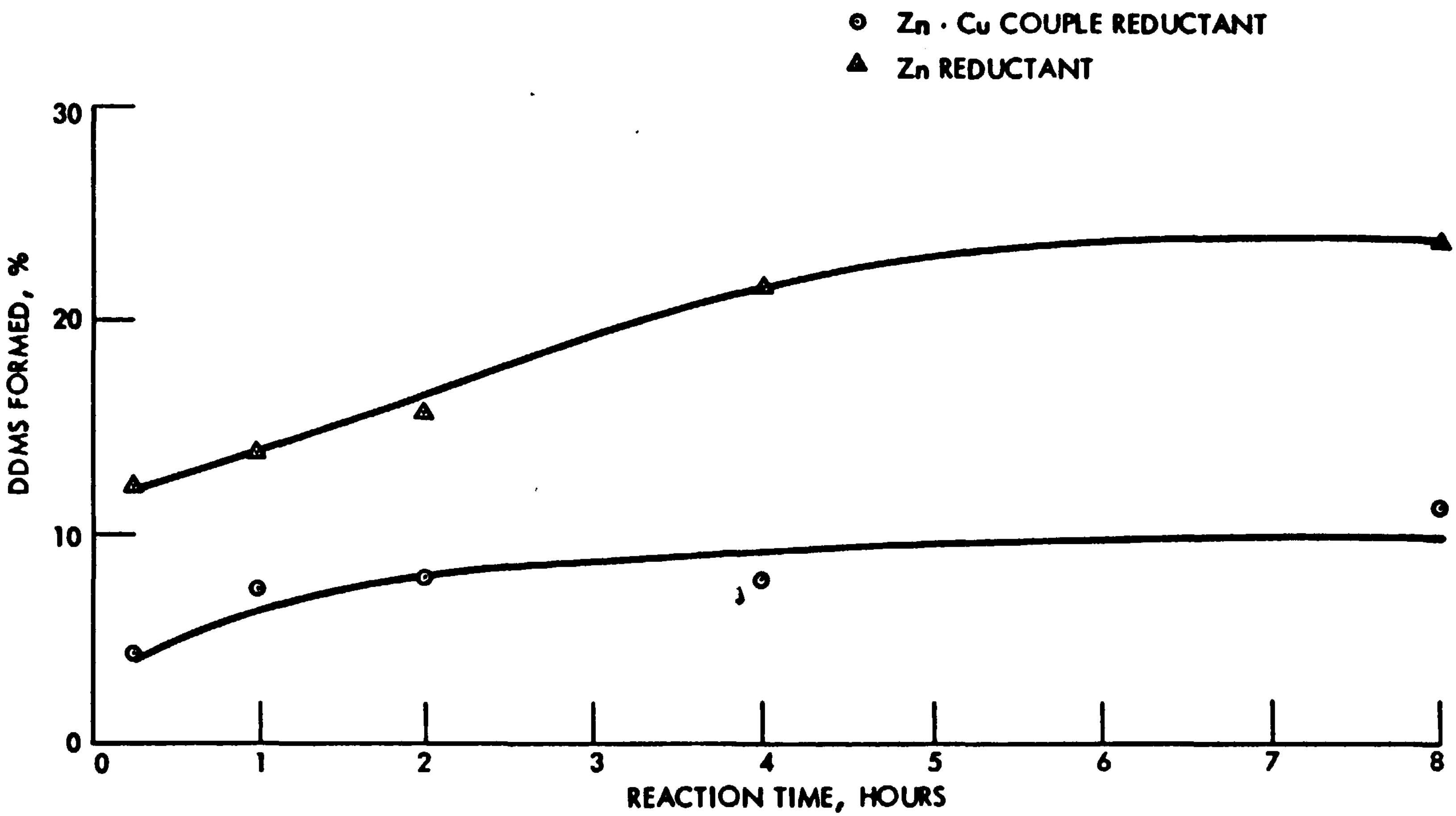

Figure 3

Rate of Formation of bis(p-Chlorephenyl) Chloroethane Product (DDMS) at 25°C When DDT Reduced with Zn. Cu Couple, or Zn Powder

Solution 0.5 N in Acetic Acid

Component	Retention Time, min	Analysis, %, after Reaction for 15 min at 25°C	
		CP Zinc Powder	CP Zinc Powder-Cu Couple
	6.8	0.1	0.1
DDEt	7.8	27.1	37.8
	10.6	0.2	0.2
	11.9	0.1	0.2
DDMU	12.8	4.0	3.4
DDMS	14.0	8.1	4.2
DDE	15.6	-	0.1
DDD	17.8	60.2	53.9
DDT	21.0	0.4	0.1

These experiments show that the zinc-copper couple gave somewhat better reduction than the zinc powder, but that the reduction was not as efficient as that obtained when the technical grade zinc powder was used in a zinc-copper couple. In an effort to determine the reason for this difference, the particle size and shape of the powders was examined, and the impurities in the materials determined by spectrographic analysis.

The particle size of the technical grade and CP grade powders, as shown from photomicrographs, was roughly equal, although the technical grade material was more nearly spherical in shape and the CP grade product tended to be elongated in shape. The particles are a nominal 5 microns in diameter. The trace metal analysis obtained by semi-quantitative arc spectra is as follows:

Metal	Analysis, %		
	Tech. Grade Powder	CP Powder	CP Granular
Iron	0.16	0.07	0.007
Aluminum	1.2	-	0.03
Lead	0.75	0.6	-
Silicon	0.01	0.005	0.16
Copper	0.005	0.02	0.0005
Indium	0.03	0.14	-
Cadmium	0.12	0.07	-
Chromium	0.02	-	-

The trace analysis gives no clear-cut explanation for the apparent effectiveness of the technical grade zinc, although the iron impurity may offer one possibility.

Tests were also run in which the amount of copper added to form the couple was varied. In these tests, the efficacy of reduction of DDT after 15 min reaction at 25°C was compared. Common to these tests was the use of 1 g DDT in 20 ml acetone solvent, 1 g of technical grade zinc dust, the addition of the copper before the acid, and the use of 10 ml of 10% acetic acid, giving a final acidity of 0.5 N. The results of the tests follow:

		Analysis, %, after 15 min Reaction at 25°C			
		Millieq. of Copper added as aq $CuCl_2$			
Component	Retention Time, min	0.1	1.0	2.0	10.0
	6.8	2.4	0.9	0.2	0.1
DDEt	7.8	29.0	56.7	52.0	37.6
	10.6	0.4	0.1	0.4	0.4
	11.9	0.1	0.1	0.2	0.3
DDMU	12.8	4.6	3.2	2.9	3.0
DDMS	14.0	9.9	4.4	3.3	1.8
DDE	15.6	-	0.2	0.2	1.3
DDD	17.8	53.8	34.4	40.2	43.8
DDT	21.0	-	-	0.6	11.9

Examination of these data show that the maximum yield of the product DDEt was shown with 1.0 meq Cu/g Zn, as well as minimal amounts of DDD and DDT. Hence this ratio of copper to zinc was used in further testing.

Since several methods for the preparation of the zinc-copper couple are mentioned in the literature, a comparison of the efficiency of the reductants to transform DDT to suitably degraded products was made. In this series, both technical grade and CP grade zinc dust reacted with 1 meq of $CuCl_2$ (1 ml of 1 N solution) were compared with a freshly prepared wet-couple, a couple prepared in wet form and then dried, and a couple prepared by elevated temperature reduction of CuO with hydrogen. The preparation of the couples follows.

Fresh, Wet Couple. This material was prepared basically by the method of Corbin, Hahn and Shechter (Reference 36). A 1 g sample of CP zinc powder was washed rapidly (~10 sec) with 3-1 ml portions of 3% HCl, then twice with 10 ml portions of water. The zinc was then treated twice with 2 ml portions of 2% $CuSO_4$ until the blue copper color disappeared (~1 min), then washed twice with 2 ml portions of water and 4 times with 3 ml washes of acetone. The sample was then used immediately.

Dry Couple. This sample was prepared by the method of Smith and Simmons (Reference 37). A 24.6 g portion of CP zinc was weighed into a flask equipped with a magnetic stirrer. Twenty ml of 3% HCl was added and the suspension was stirred rapidly for 1 min. The acid solution was decanted off and a fresh 20 ml portion of 3% HCl added and the process was repeated. A total of 4 acid washes was given the zinc. The dust was then washed 5 times with 50 ml portions of water, stirring each portion rapidly for 1 min and then decanting. The zinc was then treated twice with 40 ml portions of 2% $CuSO_4$, stirring each portion for 2 min and then decanting. The sample was then washed 5 times with 50 ml portions of water, decanting the fluid through a filter paper in a Büchner funnel so as to avoid loss of the product. The material was then washed 4 times with 50 ml portions of absolute ethanol and 5 times with absolute ether, in each case decanting through the filter so as to reclaim the product. The material was then washed into the filter funnel with absolute ether, washed three additional times with ether, and dried under water suction with a rubber dam covering the filter funnel. The material was then transferred to a vacuum desiccator and dried overnight under vacuum (P_2O_5 desiccant) before use.

Hot Reduced Couple. The third couple, prepared from an elevated temperature reduction of CuO mixed with zinc dust, was made by the method of Noller (Reference 38). A 30 g sample of CP zinc powder was blended with 2.5 g of CuO, and placed in a 50 ml, 3-necked flask fitted with a thermometer, a fritted glass inlet tube for hydrogen introduction and a gas outlet tube. The gas inlet tube was placed below the level of the metal powder bed. A constant flow of hydrogen gas was introduced into the flask during the reduction. The referenced directions stated that the reactants should be heated to slightly below the fusion point (mp Zn 419.5°C); accordingly, the mass was heated to 400°C where a steel-grey mass formed in a few minutes' reaction time. This mass was cooled, ground to a fine powder with a mortar and pestle, and stored in a vacuum desiccator over P_2O_5.

Zinc Amalgam. A zinc amalgam sample was also prepared for comparison with zinc and zinc-copper couple reductants. The method of preparation was basically that given by Fieser and Fieser (Reference 35). A 1 g sample of CP powdered zinc was treated for 5 min with 1.5 ml of 0.5 N HCl containing 0.1 g mercuric chloride, the reagent was decanted from the zinc amalgam and the material was used immediately.

In testing these materials, a 1 hr reaction time at 25°C was chosen, since the reaction did not appear to be complete at this point and therefore differences between the reductant preparations might be determined more easily. In all tests, 1 g of DDT in 20 ml acetone, 1 g reductant, and 10 ml 10% acetic acid was used (solution 0.5 N in acetic acid). The samples were stirred on a magnetic stirrer during the reaction. The results follow:

		Analysis, %, after Reaction for 1 hr at 25°C					
		Reductant					
Component	Retention Time, min	Tech Zn $+CuCl_2$	CP Zn $+CuCl_2$	Dried Zn-Cu	Fresh Wet Zn-Cu	Hot Reduced Zn-Cu O	Zn-amalgam
	6.8	0.3	0.1	0.2	0.1	0.1	-
DDEt	7.8	47.6	38.0	35.8	36.9	30.1	23.3
	9.8	0.7	0.5	0.5	0.5	0.2	0.6
	11.5	0.1	0.1	0.1	0.2	<0.1	0.2
	11.9	0.3	0.8	1.0	1.1	0.8	-
DDMU	12.6	4.0	3.8	3.6	3.8	3.0	6.3
DDMS	14.0	5.7	6.6	6.7	7.1	5.0	0.4
DDE	15.4	0.1	0.1	<0.1	<0.1	0.1	0.4
DDD	17.8	41.1	49.9	51.9	50.1	60.8	18.9
DDT	21.0	0.1	0.1	0.1	<0.1	0.1	49.9

An examination of these data shows that the couple prepared from technical grade zinc and 1 meq of $CuCl_2$ gave the best reduction. The couples prepared from CP zinc + $CuCl_2$, dried Zn-Cu, and fresh, wet Zn-Cu were all in reasonably close agreement, suggesting that these methods of preparation are about equally effective; these preparations applied to technical grade zinc may increase the activity somewhat. The hot, reduced Zn-CuO couple and the zinc amalgam were both less effective preparations for DDT reduction.

Tests were conducted to determine the shelf stability of dried Zn·Cu couple. A larger batch was made as described above and tested after one day and after 2 weeks' storage at 25°C. The results are tabulated below:

		Analysis, %, after Reaction for 24 hr at 25°C	
Component	Retention Time, min	Dried Zn·Cu After 1 day	Dried Zn·Cu After 2 weeks
	6.5	0.5	0.2
DDEt	7.6	65.7	66.5
	10.1	0.1	0.2
	11.6	0.1	0.2
	12.1	0.6	0.2
DDMU	12.8	3.9	3.5
DDMS	14.0	8.9	13.9
DDE	15.3	0.7	1.0
DDD	17.7	19.5	14.3
DDT	21.0	-	-

These results show that the reductive capability of the Zn·Cu couple is unchanged after 2 weeks' storage at room temperature.

Anhydrous Reduction System

The screening tests described earlier in this report have consisted of the examination of 1 g DDT and 1 g reductant in a solvent system consisting of 20 ml acetone and 10 ml 1.5 N acid. A voluminous precipitate quickly forms which dissolves after about 10 to 15 min reaction with the zinc reductants, and has not dissolved with other less efficient DDT-reducing systems. It was of interest in establishing the mode of reduction to determine whether the initial precipitate represented a zinc complex, or whether the flocculent mass was DDT which was consumed in the early stages of the reaction. In an experiment where the precipitate after 1 min reaction was quickly transferred to a filter funnel and separated from the liquid phase, it was found that the solid mass contained only 0.05% zinc. Since the formation of a zinc complex would be expected to give a product with 10 to 20% zinc or more, depending on the complex, it can be concluded that significant zinc complex formation is not observed. The precipitate assayed 85.8% unconsumed DDT, 11.7% DDE, 1.6% DDD and 0.3% DDEt.

Since the DDT is presumably precipitated by the water, it was of interest to examine a similar system from which the water was excluded, on the basis that the reaction might proceed more completely if the DDT were held in solution. Accordingly, a test was carried out in which the solvent system consisted of 29 ml acetone and 1 ml glacial acetic; this mix gave a final acidity of 0.5 N, the same as used in the normal screening tests. Very little reduction occurred; 50% remained as DDT, 38% was converted to DDE and only 8% DDEt was formed.

Sulfamic Acid Reduction System

It was of interest to determine whether an acid available in solid form might be used for providing the requisite acidity. A screening test with Zn-Cu couple in which 1.5 N sulfamic acid was substituted for 1.5 N acetic acid showed a somewhat lower conversion to DDEt. The experimental results are tabulated below, along with those for a typical run using acetic acid.

Component	Retention Time, min	Analysis, %, after Reaction for 24 hr at 25°C	
		1.5 N Sulfamic Acid	1.5 N Acetic Acid
	6.6	0.5	0.2
DDEt	7.8	44.5	66.5
	10.4	0.4	0.2
	11.8	1.8	0.2
	12.2	-	0.2
DDMU	12.8	6.8	3.5
DDMS	14.0	7.3	13.9
	15.2	0.2	-
DDE	15.4	-	1.0
	16.0	0.5	-
DDD	17.8	38.0	14.3
DDT	21.0	-	-

Rate of Zinc-Copper Reduction of DDT

A determination of the rate of reduction of DDT by the zinc-copper couple was carried out in an effort to establish optimal reaction conditions. In these tests, the reaction of 1 g of DDT with 1 g technical grade zinc to which 1 meq of $CuCl_2$ was added and in which the solution was made 0.5 N in acetic acid (10 ml 10% acetic acid) was studied. Samples were stirred for the reaction period with magnetic stirrers. After the reaction period, the soluble zinc, copper and chloride salts were extracted with water, and the DDT and organic degradation products extracted with 85% hexane-15% methylene chloride solution. The zinc and copper were determined by atomic adsorption, the chloride by micropotentiometric titration, and the DDT and products by the usual gas chromatographic technique. The results are given in Table II.

These tests show clearly that reduction is rapid, that a substantial amount of the zinc is consumed in the first few minutes of reaction, and that a significant amount of chloride ion is produced and acid consumed. The ratio of zinc to chloride in solution increases from 2.09 after 19 min reaction to 2.58 after 24 hrs. This increase may represent slow reaction of the zinc with acetic acid to form soluble acetates. It is of interest to note the very low quantities of copper in solution, with the quantity of copper decreasing to detection limits after about 2 hrs reaction.

The gas chromatographic results are comparable with those given earlier in this report. From the amounts of the reduction components as determined by gas chromatography, values were calculated for the amounts of chloride ion produced. These calculated chloride values are tabulated below with the measured chloride values for comparison.

Reaction Time, min	Chloride Ion from Reduction of DDT Measured in Solution, millimols	Calculated from G.C., millimols
0	-	0.12
19	4.06	4.73
30	4.65	5.44
60	4.67	5.60
120	5.50	6.19
240	5.58	6.37
480	5.86	6.55
1473	6.43	6.83

The calculated values parallel the measured values but are about 0.7 millimol higher, in most instances.

TABLE II

RATE OF CATALYZED ZINC REDUCTION OF DDT AT 25°C

Reaction Time, Min.	Zinc in Solution g	Copper in Solution g	Chloride in Solution g	pH	Analysis, %, of Component					
					DDEt	DDMU	DDMS	DDE	DDD	DDT
0	-	-	.038*	2.58	-	-	0.4	1.5	0.4	97.7
19	.381	.0010	.182	4.22	37.3	3.9	4.1	0.6	42.4	11.1
30	.450	.0008	.203	4.43	42.8	3.9	5.3	0.1	46.1	0.6
60	.431	.0003	.204	4.61	44.8	4.9	5.3	0.1	43.5	0.2
120	.569	<.0002	.233	4.72	54.6	4.0	7.1	0.1	33.2	0.1
240	.569	<.0002	.236	4.98	58.1	4.1	6.9	0.1	29.3	0.1
480	.608	<.0002	.246	5.36	60.6	3.8	8.8	0.1	25.0	0.2
1473	.688	<.0003	.266	5.56	65.7	3.9	8.9	0.1	19.5	0.3

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*Presumed to result from $CuCl_2$ added to form couple.

CATALYZED REDUCTANTS OTHER THAN ZINC

Degradation of DDT Using Aluminum-Copper System

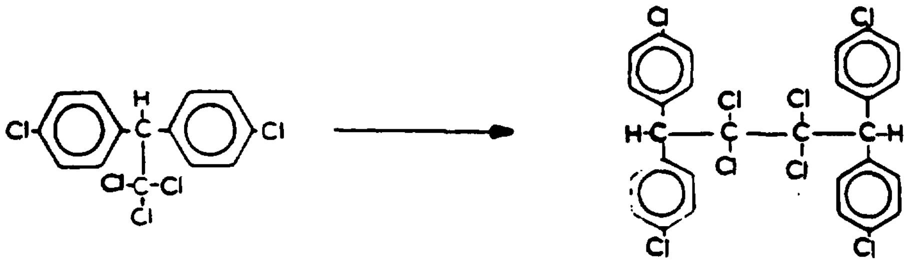
The marked increase in the reduction of DDT by the zinc-copper couple, compared to zinc alone, suggested that a reexamination of the efficacy of other metal reductants should be made, using these metals as a copper couple. In these tests 1 g of DDT was reacted with 1 g of the metal-copper couple (1 meq of aq. $CuCl_2$ added to form couple) in a solution of 20 ml acetone and 10 ml 1.5 N acid; both acetic and sulfuric acids were examined. The samples were reacted for 90 hr at 25°C.

When an aluminum-copper couple reductant was employed, two interesting results were obtained. The analysis of the sample indicated that only about 15% of the sample responded to the gas chromatograph, and that of that sample about 34% was converted to DDEt when acetic acid was used, and 64% to DDEt when sulfuric acid was the acid source. The data follow:

Acetone Soluble Component	Retention Time, min	Analysis, %, after Reaction for 90 hr at 25°C Acidified with Acetic Acid	 Sulfuric Acid
DDEt	7.7	4.8	9.2
	9.8	2.3	0.7
	11.6	0.2	0.1
	12.4	0.2	-
DDMU	13.0	0.8	0.6
DDMS	14.2	0.2	0.2
DDE	15.2	1.5	1.4
DDD	17.8	4.0	2.2
DDT	20.8	0.2	0.1
		14.3	14.5

Because of the apparently high recovery of DDEt from the reaction carried out in sulfuric acid, as well as the very low sample balance, the experiment was repeated using larger quantities. In this test, five-fold larger quantities were used and the reaction was carried out for 47 hr at 25°C. This analysis showed that of the acetone soluble material, 61% was DDEt, but that the acetone soluble fraction accounted for only 5.3% of the total sample. Undecomposed DDT represented only 0.3% of the initial sample, and DDD 0.1% of the initial sample; all of these materials are readily soluble in acetone. However, this larger sample showed a voluminous precipitate which could only be partially accounted for by the unreacted aluminum-copper couple. The precipitate was insoluble in ethanol and hexane, as well as acetone, but the major portion (other than unreacted reductant couple) was found to be soluble in warm benzene. When extracted and recrystallized, a product with a melting point of 267°C was obtained. The benzene extract weighed 86.2% of the initial weight of DDT.

The infra-red analysis showed the presence of C-Cl bonds, but no carbonyl or phenolic OH. It was hypothesized that the compound might be tetra(p-chlorophenyl)-tetrachlorobutane, formed by reductive coupling of two DDT molecules:



Elemental analysis is consistent with this hypothesis.

Analysis:	C	H	Cl
Theor, $C_{28}H_{18}Cl_8$	52.6	2.82	44.5
Found	51.8, 51.2	3.0, 2.6	42.7, 43.0

The sample was also examined by nuclear magnetic resonance spectroscopy, using $CDCl_3/CH_2Cl_2$ and hexamethyl phosphoramide as the solvents. The spectrum exhibits an aromatic pattern and a slightly broadened methinic hydrogen singlet whose relative areas are consistent with the hypothesized structure.

An examination of the literature reveals that the hypothesized compound has been prepared, and indeed has been synthesized from DDT. Insecticidal properties were claimed for the compound by Bernimolin in 1949 (Reference 39), but this finding was subsequently shown to be incorrect by Riemschneider (Reference 40). This finding was important because Reimschneider had claimed that chlorinated hydrocarbons with a melting point >200°C and a molecular weight >430 should not have insecticidal properties because of reduced lipoid solubility. The material used in these studies had been prepared by reducing DDT with hydrogen in the presence of a palladium catalyst (Reference 41). The reported melting point of 1, 1, 4, 4-tetra(p-chlorophenyl)-2, 2, 3, 3-tetrachlorobutane of

270° (Reference 40) compares well with the value of 267° obtained in this study. The tetrachlorobutane derivative does not give a gas chromatographic response under the conditions employed in this study.

It thus appears that aluminum-copper couple has almost completely degraded DDT (99.7%), giving a trace (0.1%) of DDD, and the major product 86.2% (equivalent to 95% DDT) of the tetra(p-chlorophenyl)-tetrachlorobutane. This reductant offers a different approach to pesticide degradation in that a product with apparently very low lipoid solubility can be produced by this technique; it would also be expected that the water solubility of this product would be much less than DDT. The concept of pesticide deactivation by reduced lipoid solubility may deserve further study.

Degradation of DDT Using Iron-Copper System

Reduced iron powder plus copper was also examined. One gram of DDT was reacted with 1 g of iron-copper couple (1 meq of aq $CuCl_2$ added to form couple) in a solution of 20 ml acetone plus 10 ml 1.5 N acid; both acetic and sulfuric acids were examined. The reactions were allowed to proceed for 90 hr at 25°C; the analyses of the acetone-soluble components are as follows:

		Analysis, %, after Reaction for 90 hr at 25°C	
		Acidified with	
Acetone-Soluble Component	Retention Time, min	Acetic Acid	Sulfuric Acid
DDEt	7.7	7.0	1.5
	9.8	-	2.6
DDMU	13.0	0.9	0.5
DDMS	14.0	1.4	0.2
DDE	15.4	9.4	4.5
DDD	17.8	57.3	8.2
DDT	20.8	23.9	82.6

Although the reaction proceeded to substantial breakdown of DDT to DDD when the acetic acid was used, the iron reduction does not appear to be as efficient as the zinc. However, some discrepancies in the material balance suggested additional insoluble product such as that described for the aluminum couple above.

The test using acetic acid was repeated. After removing the acetone-soluble components (equivalent to 12% of the original DDT), the solid residue was extracted with warm benzene. Evaporation of the benzene left a crystalline solid with a melting range of 265-267°C; a mixed melting point determination with authentic 1, 1, 4, 4-tetra(p-chlorophenyl)-2, 2, 3, 3-tetrachlorobutane showed no depression. The benzene extract weighed 57.6% of the initial weight of DDT (equivalent to 64% DDT).

Although the Fe·Cu couple gives substantial degradation of DDT forming the tetrachlorobutane derivative as the major product, it did not appear to be as effective as the Al·Cu couple in this test.

Degradation of DDT Using Magnesium-Copper Couple

Magnesium was re-evaluated as a reductant using added copper. One gram of DDT was reacted with 1 g magnesium-copper couple (1 meq. aq. $CuCl_2$ added to form couple) in a solution of 20 ml acetone and 10 ml 1.5 N acid; both acetic and sulfuric acids were examined. The samples were reacted for 90 hr at 25°C. The results follow:

		Analysis, %, after Reaction for 90 hr at 25°C	
		Acidified with	
Component	Retention Time, min	Acetic Acid	Sulfuric Acid
	3.8	<0.1	-
DDEt	7.7	4.3	2.1
	10.2	<0.1	<0.1
	11.7	-	<0.1
DDMU	12.9	0.7	0.6
DDMS	14.0	2.1	0.3
DDE	15.4	1.7	2.9
DDD	17.8	13.2	5.5
DDT	20.8	77.9	88.6

The Mg·Cu couple gave limited reduction of DDT. There were no discrepancies in the material balance.

Degradation of DDT Using Cadmium-Copper Couple

Cadmium was also examined as a reductant, because of its close similarity to zinc. One gram of DDT was reacted with 1 g cadmium-copper couple (1 meq. aq. $CuCl_2$ added to form couple) in a solution of 20 ml acetone and 10 ml 1.5 N acid; again both acetic and sulfuric acids were examined. The tests were of 90 hr duration at 25°C. The test results follow:

Component	Retention Time, min	Analysis, %, after Reaction for 90 hr at 25°C Acidified with Acetic Acid	 Sulfuric Acid
	3.8	<0.1	<0.1
	6.5	0.4	<0.1
DDEt	7.7	59.8	28.0
	9.8	0.8	<0.1
	11.7	<0.1	<0.1
DDMU	12.9	3.2	0.9
DDMS	14.0	7.3	3.0
DDE	15.2	0.4	2.9
DDD	17.8	10.1	5.1
DDT	20.6	18.0	60.2

Although the Cd·Cu couple gives substantial degradation of DDT, it does not appear to be as effective as the Zn·Cu reductant.

Mechanics of Reductive Degradation - Use of Zinc-Silver Couple

Tests in which a zinc-copper couple, or other metal-copper couples, were tested as reductants have been described. The use of these couples has resulted in more rapid and more complete reduction of DDT to DDEt or to tetra(p-chlorophenyl)-tetrachlorobutane. However, it had not been determined whether the copper was a specific catalyst for these reactions or whether other metals chemically similar to copper would also serve to accelerate the reduction of DDT. In a comparison, the couple formed by the addition of silver ion to zinc dust was examined as the reductant. In this test 1 g of DDT in 20 ml acetone was added to 1 g technical grade zinc dust, and the couple was formed by adding 1 meq of $AgNO_3$ solution. The solution was then acidified with 10 ml of 1.5 N acetic or sulfuric acid. The results of the analyses of products after 24 hr reaction at 25°follow. Data from a similar test with the Zn·Cu couple are given for comparison. These analyses represent the assay of the acetone soluble fractions.

Component	Retention Time, Min	Analysis, %, after Reaction for 24 hr at 25°C Zn·Ag HOAc	 Zn·Ag H_2SO_4	 Zn·Cu HOAc
	6.8	-	-	1.1
DDEt	7.8	55.5	68.4	66.5
	9.8	1.0	0.7	-
	10.6	-	-	0.5
	11.9	0.2	0.2	0.1
DDMU	12.8	9.7	11.2	3.5
DDMS	14.0	7.2	4.3	8.4
DDE	15.6	2.5	2.5	0.1
DDD	17.8	23.9	12.1	19.7
DDT	21.0	-	0.7	0.1

A deficiency in the material balances of the Zn·Ag tests suggested the formation of an acetone-insoluble product. Consequently, the Zn·Ag acetic acid test was repeated and the acetone-insoluble residue was extracted with warm benzene. Evaporation of the benzene left a crystalline solid, 0.102 g, melting in the range 226-228°C, which is as yet unidentified. The acetone-soluble portion (composed of DDEt, DDD, and DDMS) corresponded to 43% of the DDT used in the test.

In another test, the use of a couple formed by the combined addition of iron and copper salts to zinc dust was examined in an effort to further improve the efficacy of the catalyst. However, the activity was approximately the same as that obtained when the zinc-copper couple was used. The analytical results are comparable with those of the Zn·Cu reductant given in the preceding tabulation.

SECTION VII

DEGRADATION OF DDT IN SOIL

An initial series of tests were made to determine whether the zinc reduction of DDT could be carried out in the presence of an organic soil mix. In these initial tests, three samples were compared. In the first, the reaction of 1 g of zinc with 1 g of DDT in 30 ml of the dilute acetic acid-acetone medium was carried out. In the second test, 1 g of DDT + 30 ml of the solvent medium was reacted with 10 g of soil mix (no zinc was used), and in the third test, 1 g of DDT, 1 g of zinc and 10 g of the soil mix were reacted in the solvent. The soil mix was a commercial outdoor planting mix and consisted of redwood humus and nitro humus.* The samples after reaction were washed through fritted-glass filters with 100 ml of acetone. Further treatment of the organic mix in a Soxhlet extraction device revealed that no additional DDT nor degradation products were extracted. The results of analyses of the filtrates follow:

		Analysis, %, after Reaction for 24 Hr. at 25°C		
	Reductant:	Zn	Zn + Soil	Soil(Control)
Component	Retention Time, Min			
	7.0	<0.2	0.6	-
DDEt	7.8	30.3	41.1	-
	10.8	<0.2	0.4	-
	12.0	<0.2	<0.2	-
	12.5	0.4	-	-
DDMU	13.0	5.8	6.4	-
DDMS	14.0	29.1	12.8	0.5
DDE	15.6	-	0.4	6.4
DDD	18.0	34.1	38.4	3.5
DDT	21.0	-	-	89.6

The degradation of DDT proceeded in approximately the same manner in the presence of the soil mix as it did without the organic material. Clearly, the soil mix has produced no significant diminution of the degradation reaction.

Although the preceding results show that the DDT reduction by zinc was not adversely affected by the presence of an organic planting mix, it remained to be established that the reaction could be satisfactorily carried out in soil. An initial problem was the selection of a representative soil to use as a test medium.

Discussions with the Department of Agriculture, Soil Conservation Service representatives in Riverside, California, led to the selection of a Greenfield

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* Kellogg Gro-Mulch

Sandy Loam as an appropriate representative soil for California agriculture, this soil being found both in Southern California alfalfa and grain lands as well as produce and cotton fields of the San Joaquin Valley of Central California. Samples suitable for the laboratory study were obtained from a site recently characterized in an as yet unpublished soil survey (Reference 42). The characteristics of the test soil are given in Table III.

The means for practically carrying out the degradation of DDT in soil requires careful consideration. With the establishment that a small particulate reductant was the preferred mode, the geometrical or statistical factors related to practical dissemination of a pesticide and reductant can be considered.

The separate addition of the pesticide and reductant to the soil is likely to produce a system whereby the materials are not sufficiently close to effectively react. However, the dissemination of a spray in which the pesticide particle and the reductant are physically attached gives good opportunity for reaction, and indeed degradation of DDT by Zn•Cu couple in soil has been shown by this technique. If a DDT spray were applied to a field at a rate of 1 lb/acre, the number of pesticide particles per unit area and the mean distance between particles can be calculated. In this calculation, five pesticide particle sizes are shown. Insecticide dusts generally range from 1 to 10 μ in diameter. In a recent paper, Himel (Reference 43) indicated that 20 μ was an optimum size for insecticide spray droplets. A 20 μ droplet containing 1% solids (pesticide) if dried down to a single particle would theoretically yield a 4.3 μ sphere. Similarly, a 100 μ droplet, typical of boom sprayers and spray blowers (Reference 44), when dried to 1% of its volume would yield a 21.6 μ particle (although it is more likely that several smaller particles would be formed). A 100 μ particle is also shown in the calculations as an extreme value. The results of the calculations follow:

Pesticide Particle Dia, μ	Particle Density, Particles/cm^2	Mean Distance Between Particles, μ	Mean Distance Between Particles, Particle Diameters
1	1.3×10^7	2.8	2.8
4.3	1.6×10^5	25	5.7
10	1.3×10^4	88	8.8
21.6	1.3×10^3	280	13
100	1.3×10^1	2800	28

Commercial zinc and aluminum powders approximately 5 μ in diameter are available, and indeed most of the studies with zinc dust have used a nominal 5 μ dia. material. Hence, the reductant particle and an elemental pesticide particle of roughly the same size might be expected in field treatment. Since in random distribution the distance between particles is about 25 μ, the likelihood of diffusion and reaction is small. Hence, it was believed that the best opportunity for reaction would lie in the use of an integrated particle of reductant coated with or in physical proximity to the pesticide. This approach has received major attention. It has been found that 5 μ zinc dust suspensions could be readily sprayed with an air blast atomizer.

TABLE III

SELECTED CHARACTERISTICS OF GREENFIELD SANDY LOAM USED IN SOIL STUDIES

Size Distribution, %		
Sand	2 - 0.05 mm	79.8
Silt	0.05 - 0.002 mm	14.4
Clay	<0.002 mm	5.8
Size Distribution, Sand		
Very coarse	1 - 2 mm	18.8
Coarse	0.5 - 1 mm	24.9
Medium	0.25 - 0.5 mm	12.7
Fine	0.1 - 0.25 mm	17.1
Very fine	0.05 - 0.1 mm	6.3
Gravel (>2 mm), %		2.0
Moisture, %, held at tension, bar		
1/10		12.3
1/3		8.3
15		2.5
Saturation		21.9
pH		
Saturated paste		6.4
1/10 soil-water suspension		6.8
Cation exchange capacity (NaOAc)		
Meq/100 g soil		5.2
Extractable cations, meq/100 g soil		
Ca		3.1
Mg		1.0
H		2.0
Na		0.2
K		0.4
Base Saturation, %		70.0
Organic Carbon, %		0.55

The degradation of DDT in soil was examined by this technique. In the initial series, soil in 2 sq. ft. flats was treated with DDT at the rate of 1 lb DDT/acre. Three samples were treated in an initial test. In one test, a suspension of the DDT (emulsifiable concentrate) and zinc-copper couple was sprayed onto the soil, followed by acidification with dilute acetic acid. In the second test, a solution of sulfamic acid was used to acidify the reaction. In the third test, the DDT was deposited onto zinc dust particles, and the material was then applied to the soil. Reaction was then initiated by acidifying with an acetic acid spray. Specifically, the DDT in acetone solution was slurried with zinc powder and the couple formed by addition of $CuCl_2$ solution. The suspension was then dried, and suspended in water to which Triton X-100 surfactant had been added. This suspension was then sprayed onto the soil. The three samples were exposed to an out-of-doors atmosphere for 4 days and were then extracted and analyzed. The test flats were subjected to an unexpected heavy rain (~ 2.5 in.) so some DDT may have been washed away in this test.

However, it is evident that significant reduction occurred in the third sample, where a better opportunity for reaction was likely, according to the above calculation. The dissemination of the pesticide and reductant where contact occurs by chance (flats 1 and 2) led to significantly less degradation of the DDT, giving only a trace of the product DDEt. The results for the principal products follow:

		Analysis, %, after 4 days out-of-doors exposure*		
		Spray DDT + Zn·Cu Particles		
Product	Retention Time, Min	+HOAc	+ Sulfamic Acid	DDT-Zn·Cu Particle + HOAc
DDEt	7.8	trace	trace	21.4
	12.0	7.0	7.4	5.1
DDE	15.4	27.3	26.2	27.0
DDD	17.8	10.2	5.4	9.0
DDT	20.8	55.6	61.1	10.7
	29.4	-	-	20.8

Following these tests, a confirmatory test was run employing the system whereby the DDT was formed into an integral particle with the zinc-copper couple and the dispersed DDT-reductant was sprayed onto the soil. Three samples were examined, after 4 days, 7 days and 14 days out-of-doors exposure. Specifically, 0.05 g DDT (1 lb/acre on 2 sq ft flat) in acetone solution was added to 1 g of Zn·Cu couple, the solvent was removed, forming the DDT-coated reductant couple. The DDT-reductant particles were then dispersed in water to which a surfactant had been added to aid dispersal (Triton X-100), and the material was sprayed onto the soil using an air-blast type atomizer. The acidity was supplied by spraying the soil with dilute (0.5N) acetic acid. Results of the assay of the principal products after 4 days out-of-doors exposure follow:

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*Temperature range: daily maxima 60-87°F, daily minima 48-58°F
Average radiant energy (Univ. Calif. Riverside Station) 495 gm cal/cm^2
range 69-656

Product	Analysis, %
DDEt	35.4
DDE	20.3
DDD	24.7
DDT	10.1

The results after 7 days and 14 days are in general agreement with these results, although severe background interferences from the soil fractions have made a precise quantitation difficult. It is important to note, however that about 90% of the DDT has been destroyed, giving DDEt as the principal product. An adjustment of the acidity, providing the small but requisite acidity at the reaction site, is expected to remove the DDE found in this sample. It is expected, too, that the DDD will be consumed on continued reaction. Although the 7 day and 14 day results are impossible to quantitate because of interferences, it does appear that the amount of DDEt present may be decreasing with time. This may suggest a leaching or evaporation of this product. This result must be carefully determined in further experiments.

SECTION VIII

REACTIONS IN WATER

Reduction of DDT in Water

The application of the reductive technique for the degradation of DDT in waters was considered in a series of experiments. One potential application of the reductive degradation technique is with the effluent of a DDT plant in which a stream containing 100-1000 ppm of DDT may be discharged at a nominal temperature of 77°C.

In a test of the zinc-copper reductive system, 1 g of recrystallized DDT as a 25% emulsifiable concentrate was added to 2 l of water. Then zinc-copper couple prepared by the addition of 1 meq $CuCl_2$ to 1 g technical zinc powder was transferred to the reaction flask with 10 ml of acetone, and the suspension was made acid with 1 ml of concentrated sulfuric acid (solution approximately 0.018 N in H_2SO_4); the reaction was carried out with stirring for 1 hr at 75-77°C. The results of the assay follow:

Component	Retention Time, min	Analysis, %, after 1 hr Reaction at 75-77°C
DDEt	7.8	75.3
	11.8	0.4
	12.8	3.3
DDMS	13.8	10.5
	15.0	1.2
DDD	17.6	9.3
DDT	20.8	<0.2

This test indicated that the 1 hr reaction reduced the DDT level from an initial value of 421 ppm to about 1 ppm with nearly complete conversion to DDEt. Additional reaction time could be expected to reduce the DDT, DDD, and DDMS levels to even lower values.

In further tests of this reaction, a comparison was made between a sample reduced with zinc dust, a sample in which equivalent acidity was produced by the addition of HCl rather than H_2SO_4, and a test in which technical grade DDT (1 g) was dissolved in 5 ml of chlorobenzene, rather than being introduced as the emulsifiable concentrate. The Zn·Cu reductant prepared as above was employed when the DDT was added to chlorobenzene, and when the solution was made acid with HCl. The results follow:

Component	Retention Time, min	Analysis, %, after 1 hr Reaction at 75-78°C		
		Zn Reductant	HCl Acidity	Chlorobenzene Soln. of DDT
	5.6	-	-	0.6
	6.4	-	0.1	0.4
DDEt	7.8	63.0	80.4	79.0
	11.0	0.2	-	0.2
	12.0	0.2	0.1	0.2
DDMU	12.8	5.5	2.4	2.2
DDMS	14.0	8.6	8.7	4.0
	15.0	0.8	0.6	6.4
DDD + o, p'-DDT	17.8	17.7	7.7	7.1
DDT	21.0	3.8	-	-

These data again illustrate the importance of the use of the zinc-copper couple, compared to reduction with zinc alone. Reduction was efficient with both HCl acidity and the chlorobenzene addition of technical DDT; indeed, both of these conditions appear to give slightly greater conversion to DDEt with less DDD or DDMS intermediate products.

Atomic absorption analyses for zinc in the waters reveals a zinc level relatively proportional to the extent of reaction.

Reactants	Zinc in Solution, % of Zn added
DDT emuls, Zn·Cu, H_2SO_4	94
DDT emuls, Zn·Cu, HCl	70
Tech. DDT in chlorobenzene, Zn.Cu, H_2SO_4	72
DDT emuls, Zn, H_2SO_4	60

A series of tests were initiated in order to obtain information on the rate of reduction of DDT in water with the zinc-copper couple. In these tests, a two-liter sample of water was made to about 500 ppm with the emulsifiable DDT, 1 g of the Zn·Cu couple was added, and the solution made 0.018 N in HCl. The reactants were stirred continuously during the reaction. Periodically, 100 ml samples were withdrawn, extracted with 85% hexane-15% methylene chloride and assayed for DDT and degradation products by gas chromatography. The aqueous phase was analyzed for zinc and copper by atomic absorption. The results of the gas chromatography assays follow:

Component	Retention Time, min	Assay, %, after Reaction, hrs, at 23°C					
		1/4	1	2	4	24	175
DDEt	7.8	9.7	33.2	43.5	53.5	49.8	61.6
	9.8	-	-	-	0.1	0.4	1.3
	11.6	-	<0.1	<0.1	0.1	0.2	1.3
DDMU	12.8	1.3	1.5	1.8	1.7	2.3	2.9
DDMS	14.0	0.5	2.7	4.7	4.5	4.6	2.4
	15.0	1.7	0.8	0.3	0.2	0.4	1.1
	16.0	-	-	0.1	0.2	0.2	-
DDD	17.8	6.7	21.4	31.5	30.5	34.9	19.7
DDT	21.0	80.3	40.5	18.0	9.0	7.3	9.2

Analysis of the aqueous phase for soluble zinc and copper yielded the following results:

Reaction Time, hrs	Soluble Zinc, ppm	Soluble Copper, ppm
1/4	145	2.0
1	257	2.2
2	347	2.5
4	415	5.1
8	485	-

The soluble zinc assay results appear to reasonably fit a first-order reaction rate equation.

While the test shows that substantial degradation of the DDT to DDEt occurs in 4 hr at ambient temperature, the observation that the reaction has not gone to completion suggests that an improvement in either method of contacting the DDT and reductant (e.g., packed bed), or a change in reaction conditions (increased reductant or change in pH) may be necessary for improved efficiency of the reaction.

Reduction of DDT Plant Waste Samples

Other tests were conducted with waste effluent from DDT manufacturing plants. In the first test, a process stream containing about 16% solids was treated with the zinc-copper couple. The assay of the material* before treatment follows (minor peaks are neglected):

---

*Also contains 16% particulate matter, chlorosulfonic acids, and other waste material, some of which are apparently reactive with the zinc-copper couple.

Component	Concentration, mg/l
p, p' DDT	394
o, p' DDT	181
p, p' DDE	497
o, p' DDE	44

In this test, a 2 ℓ sample of the waste material was treated with 1 g of Zn-Cu couple. The sample was brought to pH 2.1 (sulfuric acid) and the reaction was carried out at 50°C (the temperature at which it is held in the plant). The assay for the major peaks follows:

	Assay, mg/ℓ, after Reaction, hrs, at 50°C						
	0	1/4	1	2	4	7	24
o, p'-DDEt (?)	0	19	19	23	19	20	22
p, p'-DDEt	0	52	56	56	73	64	65
o, p'-DDE	44	36	40	41	41	41	46
p, p'-DDE + o, p'-DDD	497	380	498	484	541	446	552
p, p'-DDD + o, p'-DDT	181	113	166	161	177	120	180
p, p'-DDT	394	262	298	283	264	296	292

These tests reveal several interesting points. First, the appearance of the product bis(p-chlorophenyl)ethane (p, p'-DDEt), and apparently also the o, p' isomer, in all samples after 15 min or longer reaction indicates strongly that the desired degradation of DDT can be achieved in the crude plant effluent, although the conditions for effective reaction must be established from further studies. Secondly, the lack of complete destruction of DDT suggests that the reagent was consumed early in the reaction, or was in some manner inactivated by the material in the crude waste effluent. The large amount of DDE (bis(chlorophenyl)-dichloroethylene) did not appear to have been substantially reduced under the conditions employed. The large amount of solids in the samples made extraction and handling difficult, factors undoubtedly responsible for the larger-than-desired scatter in the analyses. The gas chromatographic analyses were made on concentrates of hydrocarbon extracts from the waters; no attempt was made to clean up the samples by column chromatography, etc., before analysis.

A second sample was treated using a larger quantity of reagent. In this test, 10 g of reductant was used per 2 l. sample; other conditions remained the same.

Product	Assay, mg/ℓ, after Reaction time, hrs, at 50°C		
	0	1/4	6
p, p'-DDT	130	262	115
p, p'-DDEt	-	53	143
p, p'-DDD + o, p'-DDT	75	170	95
p, p'-DDE + o, p'-DDD	746	480	449
o, p'-DDE(?)	65	39	41
o, p'-DDEt(?)	-	20	61

Substantially greater production of the principal products p, p'- and o, p'-DDEt were shown in these tests, although complete consumption of the DDT was not achieved. The substantial reduction in the peak ascribed to p, p'-DDE and o, p'-DDD suggests substantial reduction of these components. It was further observed that the character of the black mass changed with continued reaction, and indeed extraction of the samples was somewhat easier as the reaction proceeded. It would appear that the continued reaction may have resulted in some reduction of the large amount of solids present in this crude stream. The high solids and attendant handling problems again resulted in larger-than-desired sample-to-sample scatter.

A low concentration DDT plant waste effluent was also examined. A 2.5ℓ sample was reacted at 75°C with 1 g Zn·Cu couple in a stirred flask. Sulfuric acid was used to adjust pH to 2.1, initially. Samples were withdrawn periodically, extracted with 85% hexane-15% methylene chloride, concentrated and analyzed.

	Assay, mg/ℓ, after Reaction time, hrs at 75°C			
	0	1/4	2	7
p, p'-DDT	0.90	0.06	-	0.11
p, p'-DDEt	-	0.84	1.20	2.53
o, p'-DDEt(?)	-	0.22	0.28	0.53
p, p'-DDD + o, p'-DDT	0.03	-	-	-
p, p'-DDE + o, p'-DDD	0.14	0.10	0.10	0.24

These results show that the DDT was being converted to the principal product DDEt. The increasing amount of DDEt with continuing reaction may indicate further reaction and extraction of DDT attached to particulate matter which did not show up in the initial analysis. The p, p'-DDEt produced after 7 hrs reaction is equivalent to 3.6 ppm p, p'-DDT in the initial sample.

Effect of pH on Reduction of DDT in Water

The tests described previously in this section have been carried out at a pH of about 2. It had not been established that this was the optimum pH; consequently, additional tests were made in the range pH = 1.0 to pH = 5.0. The reactions were run in 2ℓ distilled water in a 3ℓ beaker, with a magnetic stirring bar to provide agitation. The pH-meter electrodes were suspended in the reaction mixture and pH was controlled within ± 0.1 units by adding 1.5 N H_2SO_4 from a buret during the run. DDT (1.00 g) was introduced as an emulsifiable concentrate in xylene solution. One gram Zn·Cu couple was added at zero time and the entire mixture was extracted with 85% hexane-15% methylene chloride after 2 hr reaction at 25°C. The gas chromatographic analyses follow:

	Analysis, %, after Reaction for 2 hr at 25°C				
	pH of Mixture				
Product	pH 1.0	pH 2.0	pH 3.0	pH 4.0	pH 5.0
DDEt	27.2	44.0	27.7	10.4	-
DDMU	0.5	1.8	1.1	0.7	-
DDMS	0.7	4.7	1.2	-	-
DDE	0.5	-	0.8	1.1	1.5
DDD	9.7	31.5	26.8	23.5	5.6
DDT	61.4	18.0	42.4	64.3	92.9

Reduction of DDT in Water Using a Zinc Column

The degradation of DDT in water would be facilitated if the contaminated water could be treated by passing it through a bed of the reductant. To demonstrate feasibility, a glass tube 37 mm ID x 600 mm was filled with a mixture of 250 g Zn·Cu couple dispersed in 750 g of fine spherical glass beads; DDT (1.00 g) in 2ℓ of 10% aqueous acetic acid at 25°C was passed through the reductant-filled tube during a period of 3 hr. Effluent was collected and analyzed for products.

The effluent samples contained only traces of DDT and reduction products. The column was first drained, then 500 ml acetone was passed through. The acetone extracted 0.26 g organic material having the following composition:

Component	Retention Time, min	Analysis, %
DDEt	7.8	50.1
DDMS	14.0	2.5
	15.0	9.8
DDE	15.6	0.9
DDD	18.0	36.7
DDT	21.0	-

These results show that the Zn·Cu couple is effective as a column packing in reducing DDT, and further that the reduction products are mainly held in the column.

SECTION IX

CONTROLLED DELAYED REACTION TECHNIQUES

Although the major effort on Contract 14-12-596 has been involved in the examination of means to effectively degrade DDT to a form harmless to life, limited experimentation has been undertaken in an effort to effectively delay the degradation reaction in a controlled manner so that the pesticide can exercise its pest control function. Two basic approaches were investigated. In one, the reaction delay was introduced by applying a slowly-soluble coating to the reductant particle, thus delaying the reaction until the coating had been dissolved. This is the basic technique commonly used with the "controlled-release" fertilizers (Reference 1). The second basic technique makes use of a slow secondary reaction to provide an essential material for the DDT reduction reaction.

Several types of coatings have been investigated. Zinc-copper couple particles which are initially coated well enough so that the zinc particles will not react with dilute acid have been prepared.

One coating undergoing evaluation involves the encapsulation of the zinc-copper couple with a thin trimethyl silyl layer. In this preparation, a sample of the zinc-copper couple was mixed with bis(trimethylsilyl) trifluoroacetamide; the material was then reacted to the trimethyl silyl coating by heating at 80-90° for 1 hr, and the material was dried by tumbling after standing for 2 days. The particles when viewed under the microscope were found to be uniformly coated with a thin white layer of the coating. The coating in one experiment was about 3% by weight. When these particles were placed into dilute hydrochloric acid (pH 2.5), no bubbling was noted in 2-1/2 hours, while uncoated or poorly coated particles would react vigorously under these conditions.

Several experiments were carried out using coatings of waxes. In one experiment, a suspension of zinc dust in microcrystalline wax-benzene solution was diluted with methanol and the suspension sprayed onto a plastic-film collector. The collected "spray-dried" particles were microscopically well-coated with a layer of about 0.5μ thickness (~9% wax by weight) and the particles did not react with dilute acid. However, clumping was evident; a variation in the conditions to allow the wax coatings to harden before collection should lead to well-dispersed coated particles.

The precipitation of microcrystalline wax onto the surface of zinc powder also led to the production of material non-reactive to dilute acid but which was severely clumped. In this test, a wax-benzene suspension of the zinc powder was precipitated by adding methanol and water. Each clump appeared to contain about 100 5μ zinc particles.

A phase-separation procedure for precipitation of wax onto zinc particles was also examined. This procedure also led to the production of particles which were microscopically well-coated with microcrystalline wax, and which would not react with dilute hydrochloric acid. However, the particles were clumped into masses containing 100 or more zinc particles. In this test, a 5% solution of microcrystalline wax in 1:1 benzene-ethanol solution was prepared with a 2-1/2% suspension (w/w) of zinc dust. A 1:1 water-acetone solution was slowly added with stirring until a white precipitate of the wax could first be seen (11 cc of water-acetone solution added to 40 ml of benzene-ethanol solution of the wax). The coated particles were separated by filtration.

In other tests, zinc dust particles were fluidized by blowing air through the bed of the zinc dust and either a wax solution in benzene or a hydrocarbon oil (SAE 30 oil) dissolved in benzene was sprayed onto the particles. In neither case was the coating sufficiently impermeable to stop reaction with dilute acid.

Tests were also carried out in which paraffin wax and sulfur coatings were applied but in neither case were the coatings sufficiently uniform so that reaction of coated zinc with dilute acid would not occur. In one test, coating with a paraffin wax was achieved by layering the molten wax on water and dropping the zinc particles through the wax layer; the particles would then harden in the water and could be collected. The wax was kept molten (~ 75°C) with a heating tape attached to the cylinder holding the wax and water. The addition of surfactant was found necessary to reduce the water-paraffin interfacial tension so that gravity penetration of the interface occurred.

Thin sulfur coatings were prepared by slurrying zinc particles with a solution of sulfur in carbon disulfide and removing the solvent. A small reaction of the zinc with dilute acid was obtained, indicating incomplete coating. Sulfur coatings were thought to be promising since Powell (Reference 1) showed sulfur-coated urea gave a useful controlled-release fertilizer. However, the fertilizer coating process involved the use of molten sufur and application of this process to zinc would be expected to lead to a reaction with the reductant particle.

It appears that several methods are available for relatively simply applying a thin coating of wax or silicone to zinc particles which is sufficiently impermeable so that reaction with dilute acid does not occur. These coatings are all very slowly soluble, or can be eroded from the surface, so that the zinc can be exposed for reaction after a given period of time. The delay time can be controlled by varying the coating thickness. However, the important problem is in establishing the requisite coating thickness to give the desired reaction delay.

The second general type of delay reaction is that in which a secondary reaction is used to generate an essential reactant for the reduction reaction. The concept that was investigated makes use of the slow oxidation of sulfur to provide the requisite acidity in the delayed reaction. Initial tests of this concept were made in which a mix of sulfur, DDT and zinc dust-copper couple were exposed to an out-of-doors environment and the degradation of DDT was checked. A small amount of DDT degradation (~5%) producing DDEt as a product was noted after 2-4 weeks' exposure. In another series of tests of this concept, a humectant (glycerol) was added to keep the reaction moist. No DDEt was found after 2 weeks' exposure of these samples. In this series of tests, 1 g of DDT as a 25% emulsifiable concentrate was mixed with 1 g of Zn•Cu couple and 2 g of sulfur flowers in 10 ml of acetone. The slurry was mixed with 10 ml of 10% glycerol in ethanol and evaporated to dryness.

SECTION X

EVALUATION OF DELAYED ACTION DEGRADATION OF DDT

An examination was made of the combined system whereby the reductant particle with a coating thought to provide a reaction delay was treated with DDT and sprayed onto soil. Samples were analyzed after 4 days, 1 week, and 2 weeks out-of-doors' exposure.

In this test, zinc-copper couple particles (nominal 5μ diameter) were coated with a trimethyl-silyl coating by the process described previously. A DDT solution in acetone was added to the silyl-coated reductant and the DDT-reductant suspension was dried. The DDT-coated reductant was then dispersed in water containing Triton X-100 surfactant and sprayed onto soil. The samples were prepared with 50 mg DDT/2 sq ft flat (1 lb/acre) with 1 g of the reductant being used per flat. The acidity was provided by spraying each soil flat with 20 ml of 10% acetic acid. The soil flats contained 1800 g of the Greenfield sandy loam soil (see Section VII for description) to which 3% of the organic planting mix had been added. The results from these tests follow:

Product	Retention Time, min	Analysis, %, after Out-of-Doors Exposure, Days		
		4	7	14
DDEt	8.0	50.9	56.3	23.4
	12.0	7.0	5.9	5.1
	13.6	1.8	1.7	-
	15.2	<0.9	<0.8	-
DDE	15.6	15.8	17.6	14.6
DDD	18.4	8.8	6.7	-
	19.5	8.8	4.2	3.2
DDT	21.0	7.0	3.4	6.3
	30.0	-	4.2	38.7

Several significant results were obtained from these tests. Although the coating did not provide the desired delay, it is clear that the coated reductant DDT particle will react with substantially complete destruction of DDT (DDT 93 to 96.6% destroyed in these tests). Although the principal product appears to be bis(p-chlorophenyl)ethane)(DDEt), a decrease in this material was shown after 2 weeks' exposure.

As was mentioned earlier in this report, an apparent decrease in DDEt on out-of-doors exposure may represent vaporization of the material or leaching from the soil; the determination of the persistence of this material in the environment will require careful study. The 14-day sample showed a substantial amount of material with a 30 min gas chromatographic retention time. It is not known if this material represents a decomposition product of DDT, or whether a decomposition product of the coating was responsible for this peak.

A microscopic examination was made of DDT-coated reductant particles that had been exposed to the out-of-doors environment for 4 days. While the freshly-coated reductant particles have a white coating, these particles after exposure had turned black. Some fragments of siliceous coating were also observed. It would then appear that either a faulty coating was applied, that a reaction had occurred which destroyed the coating, or that the coating could be substantially removed in 4 days on soil. Although it was thought that the material initially tested was impervious to 2 hr exposure to dilute acid, additional tests indicated that the coating was imperfect as shown by reaction with dilute acid.

SECTION XI

DEGRADATIVE REDUCTION OF CHLORINATED PESTICIDES AND CHLORINATED BIPHENYLS

The mildly acid reduction technique discovered for DDT has also been examined for the applicability to other chlorinated pesticides and to the degradation of polychlorinated biphenyls. Complete or substantial reduction was achieved in each case.

Three series of tests were carried out. In the first, reduction of a series of chlorinated pesticides was attempted using zinc powder as the reductant. In this series of tests, the materials toxaphene, lindane, methoxychlor, dieldrin, Kelthane, chlordane, and Perthane were used. In a second series of tests, the zinc-copper couple was employed for the reduction of toxaphene, chlordane, dieldrin, endrin, aldrin and heptachlor. In each of these tests, 1 g of the pesticide dissolved in 20 ml of acetone was reacted with 1 g of the reductant (zinc dust, or zinc dust-copper couple), and the solution was acidified with 10 ml of 10% acetic acid, so that the solution was 0.5 N in acetic acid. The reactions were carried out for 21-22 hours at 25°C. In the third series of tests, the catalyzed zinc reduction of some polychlorinated biphenyls (PCB's) was investigated. For these tests, 1 g of the PCB was dissolved in 20 ml of acetone and reacted with 1 g of zinc-copper couple for 24 hours at 25°C. The solution was acidified with 10 ml of 1.5 N sulfuric acid. Analysis of the products of all tests was made by gas chromatography.

The results of these tests will be grouped according to general type of material and the data for each substance discussed.

CHLORINATED HYDROCARBONS RELATED TO DDT

Kelthane - The major peak occurred at a retention time of 24.4 min, with trace amounts of materials with 9.8, 15.0, 18.4 and 20.8 min retention also being present. Following treatment with zinc reductant, the major peak at 24.4 min disappeared, as did the trace peak at 18.4 min. The small peak at 9.8 min decreased 10-fold, while the 15 min peak increased 4-fold and the 20.8 min peak 6-fold. A major product peak at 7.6 min appeared which is presumed to represent DDEt (since Kelthane is a hydroxy-DDT, the degradation might be presumed to follow the same route as DDT). The area of the 7.6 min peak corresponds exactly with that expected for the conversion of Kelthane to DDEt. A significant product peak at 12.5 min was also observed, as well as trace peaks at 6.5, 9.9 and 10.8 min.

Methoxychlor - The major peak at 25.7 min in unreacted methoxychlor was completely removed on zinc reduction, and a new product peak at 10.6 min appeared. Moderate peaks at 20.7 and 24.2 min were also observed in the unreacted standard; zinc reduction removed the 20.7 min peak completely and reduced the 24.2 min peak to less than 1/4 of the initial area. Peaks appeared at 19.3 and 22.0 min, apparently representing the conversion of the 20.7 and 24.2 min materials.

Perthane - The major peaks in unreacted Perthane were found at 2.4, 15.3 and 17.3 min. After zinc reduction, the 2.4 min peak disappeared and the 15.3 and 17.3 min peaks decreased somewhat in size. A moderate peak at 19.6 min in the unreacted standard disappeared after reduction, as well as a minor peak at 12.6 min. A minor peak at 3.6 min decreased to about 1/4 of the initial area after reduction, while another peak representing a trace product at 13.6 min was unaffected. Product peaks with 6.4 and 7.3 min response times appeared.

HEXACHLOROCYCLOHEXANE

Lindane - The lindane standard gave a major peak at 4.2 min with a minor 1.5 min peak also being shown. After zinc reduction, both peaks disappeared.

CHLORINATED CYCLODIENE PESTICIDES

Aldrin - Aldrin is a hexachloro-hexahydro-endo, exo-dimethanonaphthalene. The unreacted aldrin sample gave a major peak at 8.9 min with minor response at 3.0 and 5.1 min. After reaction with the zinc-copper couple, the 8.9 min peak was reduced to about one-third of the initial area; the 3.0 min peak disappeared, and the 5.1 min minor peak decreased substantially in area. Substantial product peaks with response times of 6.4 and 7.3 min appeared.

Dieldrin - Dieldrin results from the epoxidation of aldrin. The gas chromatographic analyses of unreacted dieldrin, and samples following zinc and catalyzed zinc reduction, are given in Figure 4.

The principal peak from unreacted dieldrin had a gas chromatographic response time of 14.2 min; minor peaks (impurities in the commercial product)were shown at 2.8, 5.0, 7.2, 8.4, 15.0, 16.5 and 21.1 min.

Treatment with the zinc reductant decreased the major peak to 83% of the initial value, with the formation of new peaks, representing decomposition products, at 11.4 and 12.7 min. The minor peaks with 2.8, 16.5 and 21.1 min retention time disappeared, while those with 5.0, 7.2 and 8.4 min retention appeared unaffected.

When the zinc-copper couple was used, the 14.2 min peak, apparently representing the major component of dieldrin, was reduced to 28% of the initial area. The minor peaks at 2.8, 5.0, 15.0, 16.5 and 21.1 min disappeared, and the 8.4 min peak decreased to about one-fifth of its initial area. The same product peaks as observed with zinc reduction were found, and the product peak area for the zinc-copper couple, compared to the zinc reductant, was 4.7-fold larger at 12.8 min and 6.4-fold larger at 11.5 min; the 12.8 min peak is 3- to 4-fold larger than the 11.4 min peak.

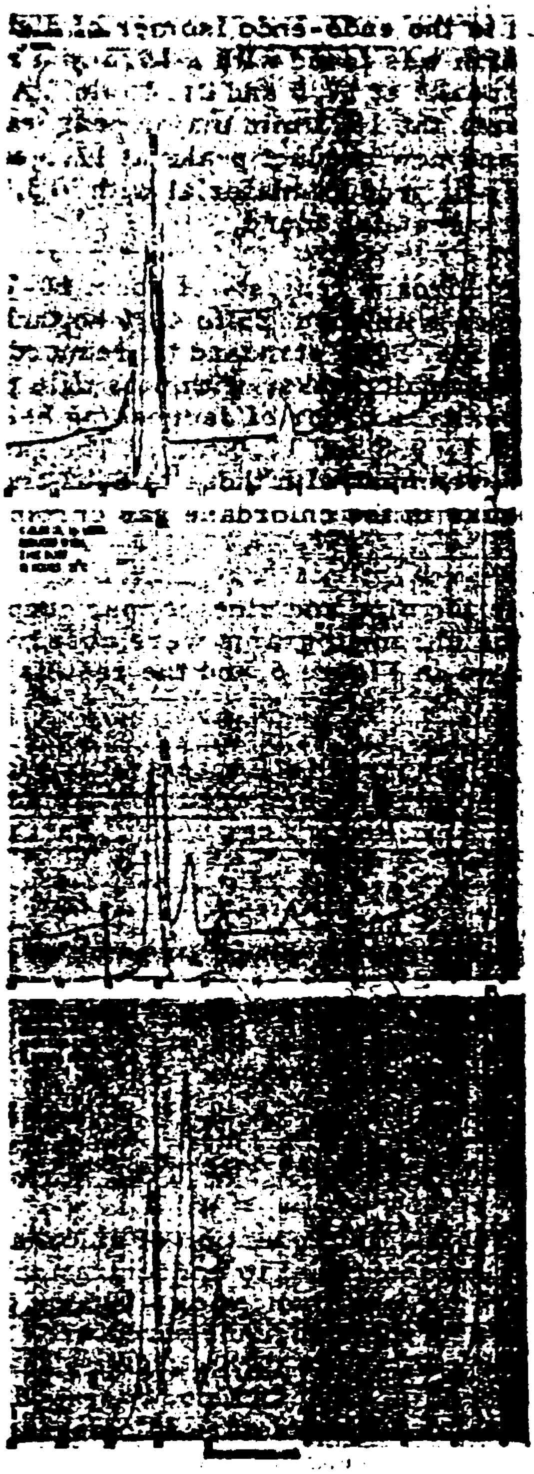

Figure No. 4. Gas Chromatographic Analyses of Dieldrin, and Dieldrin Following Reduction by Zinc or Catalyzed Zinc

Endrin - This pesticide is the endo-endo isomer of dieldrin. The major peak with unreacted endrin was found with a 15.3 min response time, with somewhat smaller peaks at 17.0 and 21.2 min. After reaction with the zinc-copper reductant, the 15.3 min major peak was reduced to about 10% of its initial area and new product peaks at 12.5 and 13.8 min were shown. Trace quantities of product material with 6.3, 17.4, 20.7 and 21.5 min retention time were also found.

Chlordane - Technical chlordane consists of about 60-75% octachlorahexahydro-methanoindene, with about 25 to 40 % heptachloro-, hexachloro-, and enneachloro-compounds. The standard (unreduced) sample gave a number of gas chromatographic peaks, with no single peak giving a major response. The peaks in order of decreasing height occurred at 11.6, 12.7, 6.9, 8.4, 6.1, 9.8 and 17.0 min. The gas chromatographic results are in general agreement with those of Saha and Lee (Reference 45), who reported 14 peaks in the chlordane gas chromatographic record.

Following reduction with the zinc and zinc-copper couple reductants, significant changes in the chromatograms were observed. These chromatograms are shown in Figure 5. and the results may be summarized.

Retention Time, Min	Peak Area ($\propto$ Concentration) for Reduced Sample as Compared to Unreacted Standard	
	Zinc Reductant*	Zn·Cu Reductant
11.6	<25%	<10%
12.7	~60%	~ 0
6.9	0	0
8.4	~25%	~0
6.1	little change	little change
9.8	~75%	~60%
17.0	~10%	0
15.0		(new large reductant peak formed)

It is thus obvious that substantial reduction of chlordane has been achieved, the peak area (proportional to concentration) appearing to have been reduced to 10% or less (indicating ~90% or greater reduction) for the four largest peaks in the chlordane structure.

Heptachlor - This compound is a heptachloro-tetrahydro-endomethanoindene, and hence is related in structure to chlordane. The gas chromatographic analyses of unreacted heptachlor, and heptachlor reduced with the zinc-copper couple, are shown in Figure 6. The heptachlor standard gave major peaks at 7.3 and 12.0 min, with trace amounts responding at 5.2, 13.0 and 13.7 min.

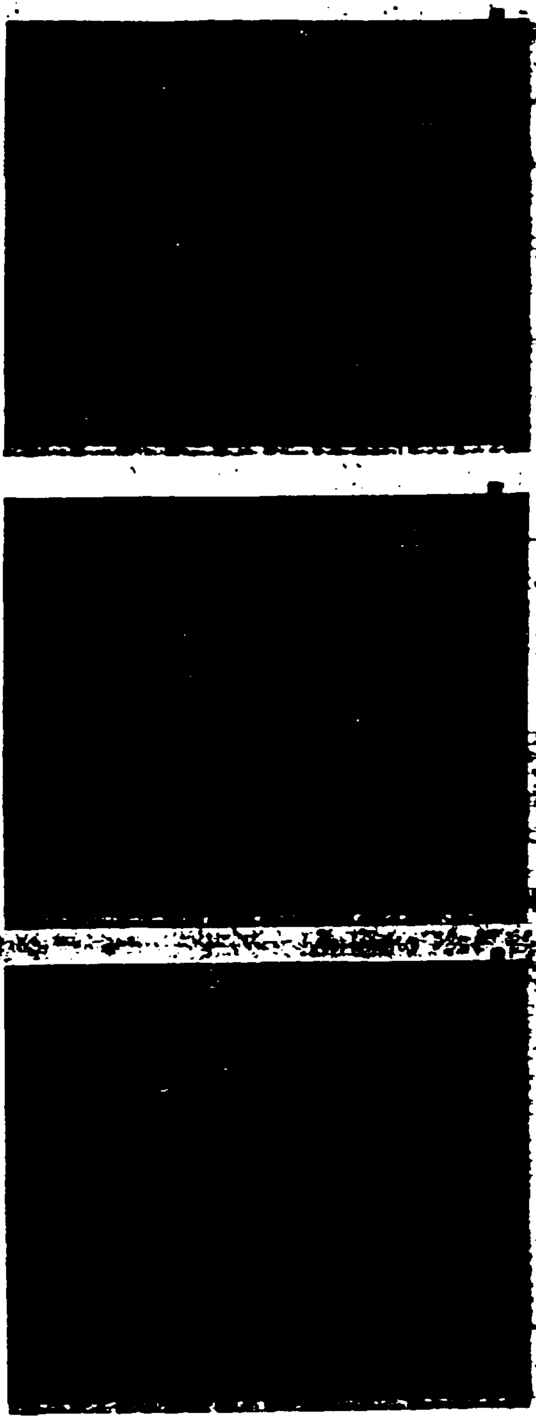

Figure No. 5. Gas Chromatographic Analyses of Chlordane, and Chlordane Following Reduction by Zinc or Catalyzed Zinc

Endrin - This pesticide is the endo-endo isomer of dieldrin. The major
peak with [illegible] times
with somewhat [illegible] ion with
the zinc-copp [illegible] d to about
18% of its [illegible] in were
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Chlordane - [illegible] chloro-
hexahydro [illegible] xachloro-,
and onmeschlo [illegible] gave a
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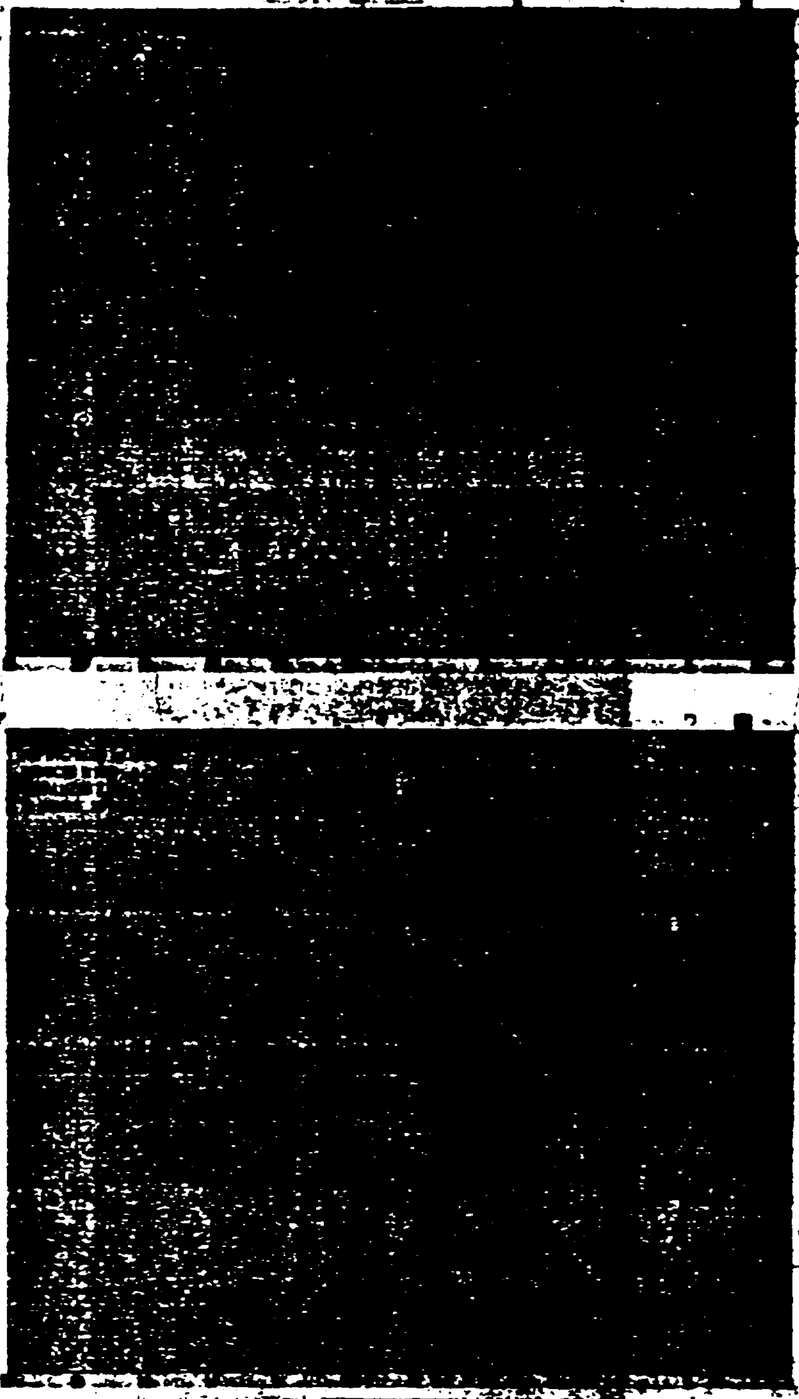

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Figure No. 62 Gas Chromatographic Analyses of Heptachlor, and Heptachlor Following Reduction by Catalyzed Zinc

After reaction with the zinc-copper couple, the major peak at 7.3 min was reduced to 2% of the unreacted value, and the 12.0 min product was reduced to 10% of the initial value; the 7.3 min peak was about 4.4-fold larger initially than the 12.0 min peak and therefore must be the major component. The minor peak at 13.7 min disappeared after treatment with the reductant, but the 5.2 and 13.0 min peaks increased in area. The 5.2 min product was 4-fold greater and the 12.0 min material 25-fold greater after reduction; it appears probable that these peaks represent decomposition products.

CHLORINATED CAMPHENES

Toxaphene - Toxaphene is produced by chlorinating camphene to 67-69% chlorine (about 8 chlorine atoms/camphene molecule).

The gas chromatographic traces for unreacted toxaphene, and toxaphene reduced either with zinc, or zinc-copper couple, are given in Figure 7.

The standard (unreduced) sample gave a very complex gas chromotographic curve with the principal peaks, in order of decreasing height, being observed at 16.3, 21.2, 19.5, 18.0 and 15.1 min.

When the zinc reductant was used, all of these peaks disappeared and a series of new peaks developed with retention times of 2 to 10 min. The use of the zinc-copper couple reductant resulted in the formation of several peaks with retention times of less than 4 min, with essentially no response at longer retention times. It is clear from these results that the use of either the zinc or zinc-copper couple appeared to destroy the initial toxaphene structure, and that the zinc-copper reductant appeared to give products with shorter gas chromatographic retention times than the zinc reductant; the products obtained with the zinc-copper couple are presumably more volatile or smaller molecules than those obtained from zinc reduction.

EXTENT OF CHLORINATED PESTICIDE REACTION

These data show clearly that all of the chlorinated pesticides tested were substantially or completely degraded by the zinc or zinc-copper couple reducing systems after 21 hr at 25°C. However, neither the extent of degradation nor the degradation products have been identified.

In an effort to establish the extent of reaction, the soluble chloride was extracted from the products of the reaction of the Zn·Cu couple with toxaphene, dieldrin, aldrin, endrin, chlordane and heptachlor. In addition, the reacted zinc in solution was determined by atomic absorption. The chloride was analyzed by a micro-potentiometric titration technique.

The water soluble chloride results follow:

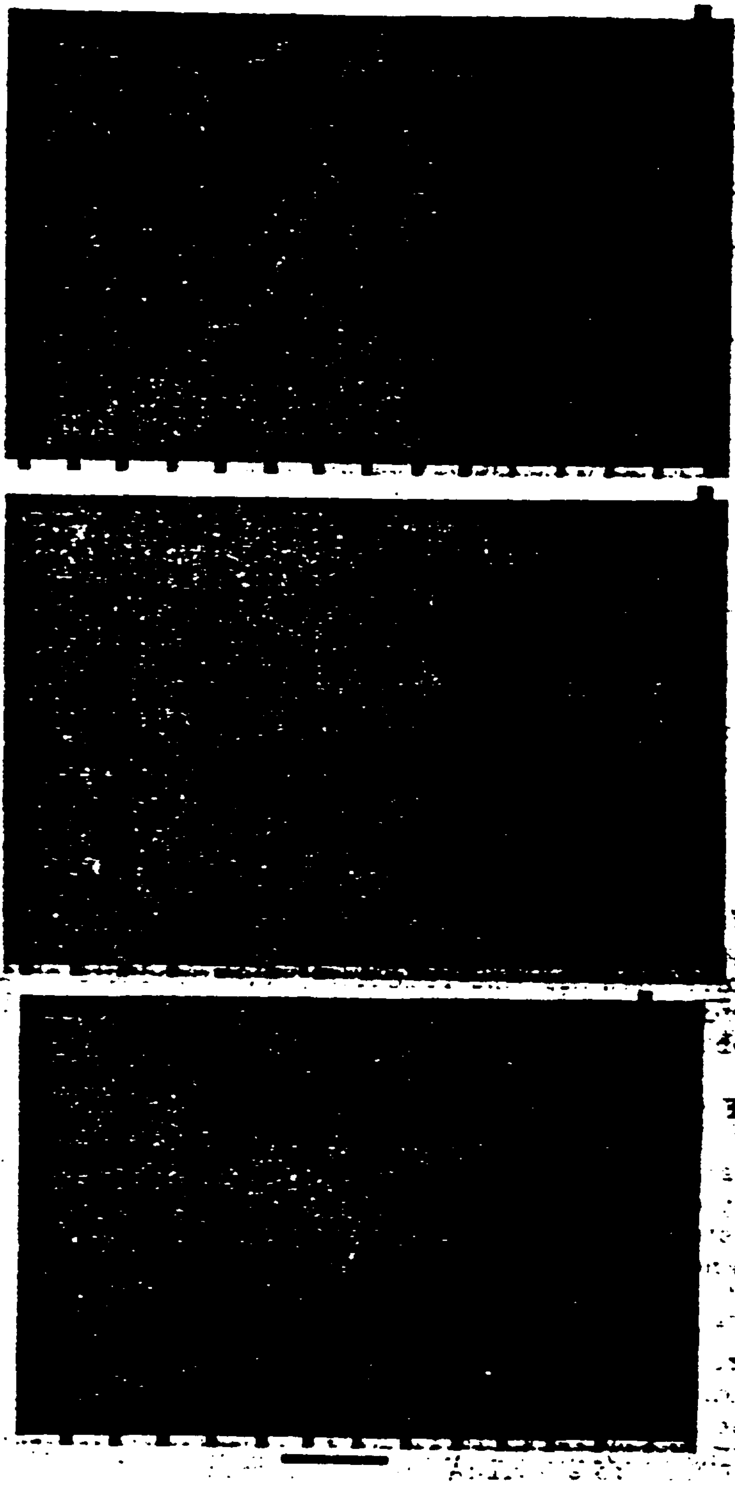


Figure No. 7. Gas Chromatographic Analyses of Toxaphene, and Toxaphene Following Reduction by Zinc or Catalyzed Zinc

Pesticide	Soluble Chloride, g	% of Theoretical Chloride
toxaphene	0.425	61.6
chlordane	0.205	29.6
dieldrin	0.106	19.0
heptachlor	0.169	25.3
endrin	0.141	24.8
aldrin	0.123	21.0

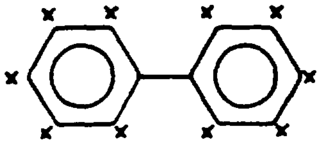
These results show a substantial removal of chloride from toxaphene (>60%), but a much smaller amount of chloride released from the other pesticides investigated. However, molecular changes can be made without the release of soluble chloride, and the zinc results suggest complete reaction of the pesticides.

Pesticide	Soluble Zinc Equiv. x 10^{-2}	Theoretical Chloride Equiv. x 10^{-2}	Ratio: $\frac{\text{Soluble Zn}}{\text{Theor. Cl}}$
toxaphene	2.18	1.94	1.12
chlordane	1.93	1.95	0.99
dieldrin	1.64	1.58	1.04
heptachlor	1.81	1.87	0.97
endrin	1.49	1.61	0.93
aldrin	1.66	1.64	1.01

It may be concluded that all of the chlorinated pesticides examined have been substantially degraded by the reductive degradation technique. However, the chemically stable cyclodiene pesticides such as dieldrin are expectedly more stable than the chlorinated camphenes (toxaphene) or the closer relatives of DDT (Kelthane, methoxychlor). The general applicability of the reductive degradation technique for chlorinated pesticides is nevertheless shown.

POLYCHLORINATED BIPHENYLS (PCB'S)

PCB's - The PCB's are a series of polychlorinated biphenyls and terphenyls chlorinated to contain 20 to 68% chlorine. The general formula would be (biphenyl), (Reference 46).



x = possible chlorine sites

These materials are used extensively for industrial purposes such as heat transfer fluids, printing inks, hydraulic fluids, dielectrics, protective coatings, etc., and hence find their way as industrial waste into rivers, lakes and estuaries.

Three samples were examined. The samples and their basic composition follow:

Material	Basic Structure	Chlorine, %
Aroclor 1268	biphenyl	68
Aroclor 1248	biphenyl	48
Aroclor 1232	biphenyl	32

The results of the reduction of each of these samples can be described.

Aroclor 1268 - The gas chromatographic structure of this compound is complex, with at least 8 peaks being shown in unreacted Aroclor 1268. This finding is in general agreement with Reynolds (Reference 47) and Risebrough, et al (Reference 48); Reynolds reported as many as 14 peaks in Aroclor chromatographic analyses. However, upon reaction with the zinc-copper couple for 24 hr at 25°C, a significant reduction of many of these peaks was observed.

Retention Time, Min	Peak Area ($\propto$ Concentration)	
	Unreacted Standard	Reduced with Zn·Cu Couple
22.1	0.11	0.11
24.5	0.22	0.14
26.1	0.07	0.09
28.9	1.00	0.58
31.3	0.47	0.44
32.8	0.18	0.12
35.7	1.15	0.64
37.9	0.28	0.25

It is thus apparent that the two major peaks (28.9 and 35.7 min) have been reduced by 42 and 45%, indicating significant reaction. Reduction in the area of the peaks at 24.5 and 32.8 min was also observed, while no significant change appeared to be observed in the small peaks at 22.2, 26.1, or the moderate sized peaks at 31.3 and 37.9 min. It is believed that a modification of reaction conditions will provide more extensive degradation of this material.

Aroclor 1248 - The gas chromatographic trace of this compound appears to be more complex than Aroclor 1268, at least 16 peaks being observed in the trace of the unreacted compound. The chromatographic structure is highly complex, with many of the peaks not being completely resolved, so no effort was made to integrate the curve. However, the unreacted sample analysis and the results after reduction with the zinc-copper couple can be compared. The peaks will be listed in the order of decreasing height.

Retention Time, Min.	Peak Area($\propto$ Concentration) of Reduced Sample Compared to Unreacted Standard
8.5	~ Same
11.6	~ 0
6.7	~ 10%
9.3	~ 0
5.0	~ 10%
7.1	~ 0
9.8	~ 0
12.6	~ Same
5.6	~ 0
13.4	< 25%
3.8	~ 0
2.7	< 33%
29.8	Large Product Peak Appeared
1.7	Small Product Peak Appeared

It is thus obvious that many of the peaks were completely, or nearly completely, removed indicating that many of the isomeric forms have been effectively degraded by the reductant couple. Again, modification of the reducing conditions is expected to lead to more substantial degradation of this material.

Aroclor 1232 - Similar to Aroclor 1248, a complex gas chromatographic trace with 15 peaks was obtained with unreacted Aroclor 1232. The structure after reaction of the compound with the Zn•Cu reductant can be qualitatively compared. The peaks again will be listed in the order of decreasing height.

Retention Time, Min.	Peak Area ($\propto$ Concentration) of Reduced Sample Compared to Unreacted Standard
1.7	~ Same
2.3	~ Same
3.6	~ 33%
1.1	~ 50%
2.6	~ 25%
4.9	~ Same
6.6	~ 50%
3.2	~ 33%
5.4	~ 50%
7.0	~ 50%
8.3	~ Same
9.2	~ 33%
9.6	~ 33%
11.4	Larger (Product Peak?)
12.4	~ Same

Again it appears that many of the peaks have been reduced substantially in area, and it is believed that more complete reduction can be achieved. The very complex nature of the gas chromatographic trace has made the peak area comparison very difficult.

SECTION XII

ANALYSIS OF STUDIES

The studies summarized in the preceding section had as their objective the determination of the feasibility of a concept of controlled destruction of field-applied pesticides such as DDT. It will be the objective of this section to attempt to analyze these data and determine whether feasibility has been established.

The degradation studies have led to two basic systems for destruction of DDT, with at least three apparently practical reductant systems. Major emphasis was put on the catalyzed zinc reducing system. This process has been shown to reduce DDT to the principal product DDEt in reasonable times at room temperature. The product DDEt appears to be a safe product to the environment on the basis of acute toxicity data; it is believed that the product will not exhibit the reproductive effects shown by DDE (and DDT), but this remains to be demonstrated.

A major question in determining the practicality of the degradation of a field-applied pesticide is concerned with the means for carrying out the reaction in the field. While many reactions can be carried out in the laboratory, the practical application to the field may be unduly difficult or impossible. In Section VII it was shown that the best opportunity for reaction would appear to involve the formation of an integral particle of DDT and the reductant. The separate application of the pesticide and the degradative treatment would require a migration or diffusion of a soluble species (e.g., emulsified DDT) to the particulate reductant, and the probability of this occurring for all of the pesticide droplets is very low. However, by forming the reductant and pesticide into an integral particle, the probability of reaction is made much larger and, as has been demonstrated, a 90-95% destruction of the DDT in soil was achieved in 4 days out-of-doors' exposure. A second advantage may be seen in the integral particle approach. Effective reduction appears to require a mildly acidic condition. However, the integral particle concept will allow the acidity to be added only at the point of reaction, rather than being spread over the field, where an approximate pH 2 condition might lead to plant damage as well as requiring an excessive quantity of acid.

It would be well in considering the integral particle concept to determine whether DDT dispersed in this form would be effective as a pest control agent. LaMer and Hochberg (Reference 49) investigated the killing properties of carefully controlled DDT aerosols on mosquitoes and flies and concluded on the basis of aerodynamic capture, settling velocity, and related factors that a 5-10 micron aerosol was to be preferred. It therefore appears that the size of the particle produced in the integral particle concept is in the approximate size range for optimal pest control action; the size is in line also with more recent studies by Himel (Reference 43), suggesting an approximate 20 micron insecticide aerosol as being optimal.

Although major effort was expended in investigating the catalyzed zinc reductant system, the more recent results using catalyzed aluminum or iron reductants offer a new and potentially attractive approach to pesticide degradation. The approach is basically to produce a high molecular weight degradation product which is not lipoid soluble. Hence the material would presumably not be accumulated by life forms in fatty tissues. Further advantages of this potential process include a sharp decrease in the calculated amount of reductant metal required, and the release of different metal ions as reduction products. Some of the factors involved in a comparison between the three reductant systems can be tabulated:

	Zn-Cu Couple	Al-Cu Couple	Fe-Cu Couple
Principle:	Remove chlorine to form non-toxic product	Forms insoluble non-reactive product	Forms insoluble, non-reactive product
Theoretical: equiv. reductant/mol DDT	3	1	1
Theo. Cost* cents/lb DDT	5.5	1.0	0.2
Theor. lb metal ion/lb DDT	0.28	0.025	0.052
Concentration Effect	Has been shown effective at 1 ppm DDT in water	Probably free-radical mechanism; may require concentration for reaction in water	Same as Al-Cu couple

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*Based on zinc dust at $0.20/lb, Al powder at $0.40/lb, Fe powder at $0.04/lb.

The use of the aluminum and iron reductants would appear to offer no environmental problems, and indeed the salts produced would probably hydrolyze and the insoluble hydrous oxides be precipitated. The copper catalyst appears to be reduced to the insoluble metallic form and would offer no contamination problem.

The use of a zinc reductant can be further analyzed on the basis that soluble zinc chloride would be formed. If it is assumed that DDT is applied to a field at 1 lb/acre, then 0.276 lbs of zinc is theoretically required to react with it. If all of the zinc is soluble and were released at the time of an irrigation equivalent to 1 in. of rain, or an equivalent rain, and the zinc were washed into a reservoir or river with no dilution of the soluble salt, then 1.2 mg/l of zinc would be found. In practice, it is believed that because of water stream dilution, salt adsorption, rate of release, etc., the amount of soluble zinc found in the water would be much lower than 0.1 mg/l.

The zinc ion which might be introduced into the water from the use of the reductive degradation process for waste water treatment can be similarly examined. If a million gallon per day water source is treated, the theoretical zinc ion in the water as a function of the DDT level would be as follows:

DDT level, mg/l	Zinc ion in water, mg/l, calculated, for 1 MGD stream
1.0	0.3
0.1	0.03
0.01	0.003

The environmental effect of the soluble zinc resulting from DDT degradation can be further analyzed.

The zinc content of water from the preceding calculations is much lower than the 5 mg/l permissible criteria for water supplies (Reference 50). However, it appears that lower zinc concentrations are desired if damage to the fish population is to be avoided.

Recent studies by Brungs (Reference 51) indicate a decreased egg production rate of the fathead minnow when the zinc concentration of water is raised from 0.03 to 0.18 mg/l. In another study, Crandall and Goodnight (Reference 52) found that 2.3 mg/l of zinc ion had a deleterious effect on guppy growth and mortality.

Other studies indicate the complex nature of the toxic effect of zinc to fish. Skidmore (Reference 53) reports the toxic effect of zinc is dependent upon the species, age, acclimatization, hardness of the water, dissolved oxygen concentration, and temperature. Similarly, Mount (Reference 54) found that there was a relationship of pH and hardness to the zinc toxicity to minnows, the toxicity being greater at a pH of 8 and hardness of 50 ppm than at pH 6, hardness 200 ppm. The most severe toxic effect reported in the Skidmore paper involved a referenced test where only 46% of rainbow trout fry survived 28 days in water containing 0.01 mg/l of zinc ion. This level is well below the zinc level commonly found in natural waters in this country. As an example, O'Connor, Renn and Wintner report the average zinc level in a series of Maryland rivers was 0.05 mg/l and the observed zinc levels fall in the range 0.015 to 0.095 mg/l (Reference 55). These levels appear representative of other areas of the country, according to citations in this paper. In contrast, the Mount paper lists median tolerance limits for the fathead minnow to zinc ion from 6.2 mg/l to 35.5 mg/l, depending on pH and hardness.*

These data do not give a clear answer as to whether the use of the zinc reductant would offer an environmental problem to fish. Potential treatment applications of DDT plant wastes may well involve low-volume, high-concentration streams from which the zinc salt may be precipitated (as hydroxide, carbonate, phosphate) as well as extensively diluted before being wasted. Hence the concentration of zinc ion entering the waters may be very low. Similarly, the soluble zinc salts in agricultural run-off may be very low because of adsorption, dilution, etc.

An important aspect of any program of development and evaluation of the zinc reduction technique for degradation of field-applied pesticides would be the measurement of the soluble zinc ion in the run-off waters. The development of the catalyzed aluminum or iron reductant systems would not appear to offer problems of fish toxicity under reasonable conditions of use.

Although the insecticidal properties of the combined reductant-DDT particle have not been determined, it would appear that the action of the DDT should not have been affected.

In summary, it appears that the basic process for DDT degradation is effective, that a practical means for particle dissemination and reaction has been discovered, that the reactions are economically feasible, and that the products produced by one or both of the basic processes are expected to be harmless to life forms unless conditions resulted in sufficient zinc ion build-up to damage fish. In short, it is believed that the feasibility of the degradative process has been demonstrated.

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*Mount points out that his data are in disagreement with most published work, but further states that this would appear to be because of his use of a flow-through test system, which keeps precipitated zinc in suspension, rather than the static test system employed by others. It should be noted that the flow-through system would appear to be a much better simulation of real-life behavior.

The feasibility of reaction delay techniques can also be examined. Two basic processes were suggested for delaying the reductive reaction, one involving the slow solubility of a coating, the other the delayed generation of an essential ingredient for the reaction.

The use of slowly-soluble coatings such as microcrystalline wax should provide a coating that can be readily and cheaply applied. The reaction delay period should be controllable through the coating thickness. The background of experience in controlled-action fertilizers suggests that this process can be readily developed for practical use, although the precise definition of coating thickness to delay the reaction for a given time must be established from further studies. The effect of erosion by soil particles with wind movement, etc., must be established also.

Although little data has been obtained as yet on the delay technique involving the slow oxidation of sulfur to provide the requisite acidity, the concept has merit because it would provide a means for generating the acidity at the reaction site. Soil sulfur is both a relatively cheap material and one used extensively for agricultural purposes so that no deleterious effect on the plant would be expected. A major problem with this concept would appear to be in devising means to control the reaction to give a stated delay time; the coating technique would appear to be more readily adaptable to delay time regulation.

Although the test of the combined degradation process and delayed action technique did not give the requisite reaction delay because of a faulty coating, the observed 90-95% DDT degradation using the integral particle of DDT and coated reductant indicates strongly that the reaction will go in the predicted manner, given an initially impervious coating.

A further factor in establishing the feasibility of the generalized concept of controlled destruction of DDT is concerned with the method of dissemination of the material. It has been shown that the integral DDT-reductant particle can be effectively sprayed from a conventional air-blast atomizer. Therefore it would appear that little difficulty should be experienced in disseminating the material from spray units now used. Since the size range is similar, no major problems are envisioned in formulating controlled-degrading DDT dusts.

Although this feasibility effort has been directed mainly to the application of DDT to the field, it is believed that the efforts described in this report show that waste treatment of DDT in water can also be feasible, as well as the application of the reductive degradation technique to other chlorinated pesticides and the polychlorinated biphenyls (PCB's).

In summary, it is believed that the studies described in this report demonstrate clearly that a controlled destruction of field-applied DDT is a feasible process, that the degradation can be accomplished in soil, and that the process appears to be economically practical. The limited studies also show the general application of the process to the treatment of other chlorinated pesticides, and the PCB's (polychlorinated biphenyls) industrial pollutants. The potential for reductive treatment of waste water laden with DDT was also shown.

SECTION XIII

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SECTION XV

PATENTS AND PUBLICATIONS

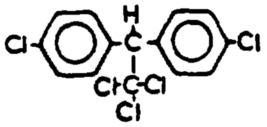
Patent applications are being prepared for the significant findings on this program. Technical papers describing the findings on the chemistry of DDT will be prepared by the authors of this report.

SECTION XVI

GLOSSARY

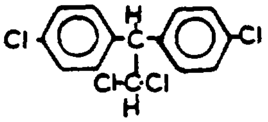
CHEMICAL FORMULAS OF PESTICIDES AND DEGRADATION PRODUCTS

DDT



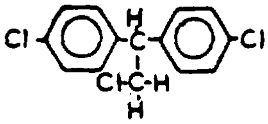
2, 2 bis(p-chlorophenyl)-1, 1, 1-trichloroethane

DDD (TDE)



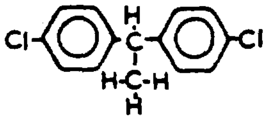
2, 2 bis(p-chlorophenyl)-1, 1-dichloroethane

DDMS*



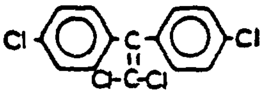
2, 2 bis(p-chlorophenyl)-1-chloroethane

DDEt



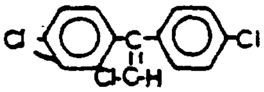
1, 1 bis(p-chlorophenyl) ethane

DDE



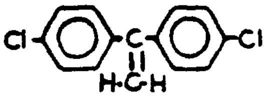
2, 2 bis(p-chlorophenyl)-1, 1-dichloroethylene

DDMU (TDEE)



2, 2-bis(p-chlorophenyl)-1-chloroethylene

DDNU



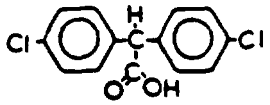
1, 1-bis(p-chlorophenyl) ethylene

*Coding of compounds used by Menzies, "Metabolism of Pesticides," (Reference 17).

GLOSSARY

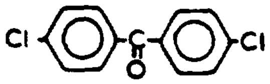
CHEMICAL FORMULAS OF PESTICIDES AND DEGRADATION PRODUCTS

DDA



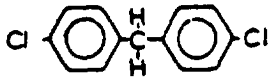
bis(p-chlorophenyl)acetic acid

DBP



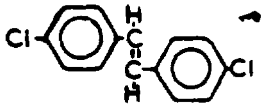
4, 4'-dichlorobenzophenone

DDM



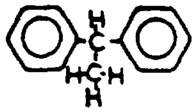
bis(p-chlorophenyl)methane

DCSt



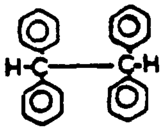
trans 4, 4'-dichlorostilbene

DPEt



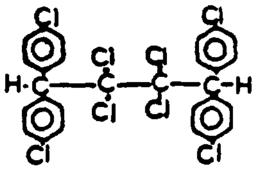
1, 1-diphenylethane

TPEt



1, 1, 2, 2-tetraphenylethane

TTTB

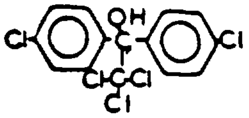


1, 1, 4, 4-tetra(p-chlorophenyl)-2, 2, 3, 3-tetrachlorobutane

GLOSSARY

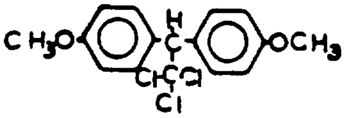
CHEMICAL FORMULAS OF PESTICIDES AND DEGRADATION PRODUCTS

Kelthane



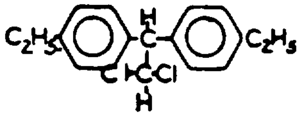
1, 1-bis(p-chlorophenyl)-2, 2, 2-trichloroethanol

Methoxychlor



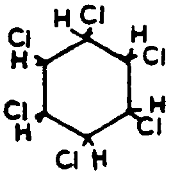
2, 2-bis(p-methoxyphenyl)-1, 1, 1-trichloroethane

Perthane



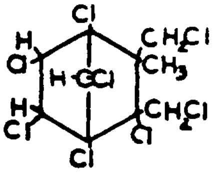
2, 2-bis(p-ethylphenyl)-1, 1-dichloroethane

Lindane



γ-1, 2, 3, 4, 5, 6-hexachlorocyclohexane

Toxaphene

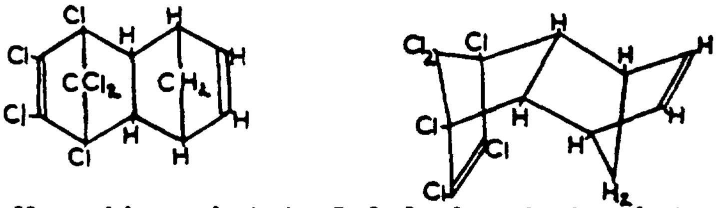


Chlorinated Camphene

GLOSSARY

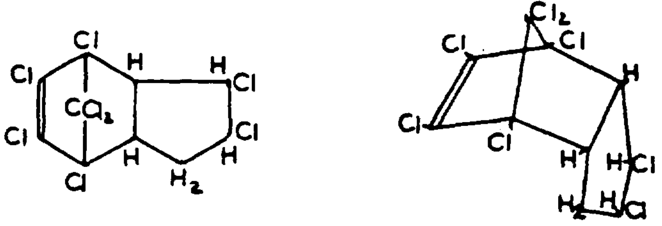
CHEMICAL FORMULAS OF PESTICIDES AND DEGRADATION PRODUCTS

Aldrin



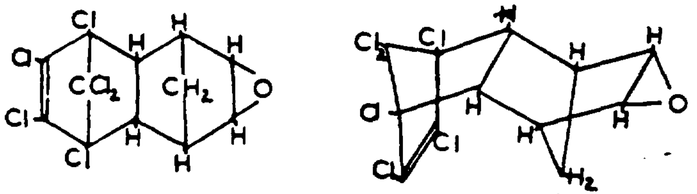
1, 2, 3, 4, 10, 10-Hexachloro-1, 4, 4a, 5, 8, 8a-hexahydro-1, 4-*endo*, *exo*-5, 8-dimethanonaphthalene

Chlordane



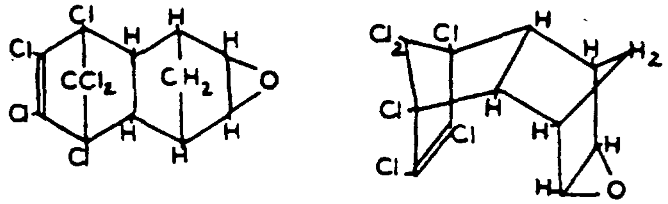
1, 2, 4, 5, 6, 7, 8, 8-Octachloro-2, 3, 3a, 4, 7, 7a-hexahydro-4, 7-methanoindene

Dieldrin



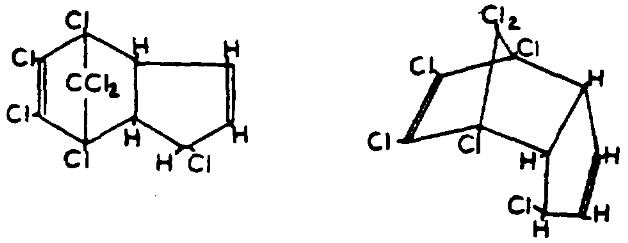
1, 2, 3, 4, 10, 10-Hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1, 4-*endo*, *exo*-5, 8-dimethanonaphthalene

Endrin



1, 2, 3, 4, 10, 10-Hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1, 4, -*endo*, *endo*-5, 8-dimethanonaphthalene

Heptachlor



1, 4, 5, 6, 7, 8, 8-Heptachloro-3a, 4, 7, 7a-Tetrahydro-4, 7-*endo*methanoindene

SECTION XVII

APPENDIX A

PRODUCT ISOLATION, IDENTIFICATION AND CHARACTERIZATION

An important technical problem in this investigation was the identification of the degradation products. Two generalized approaches were used in this study. First, degradation samples were split into fractions by chromatographic or other means and the separate fractions characterized by such techniques as infrared, nuclear magnetic resonance, and elemental analyses. Secondly, where degradation processes could be predicted, compounds were procured or synthesized for analysis and comparison with the gas chromatograph results.

Gas Chromatography Analyses

The analytical chemistry of the DDT and its degradation products was accomplished by a gas chromatography technique. The analyses were made with a Perkin Elmer Model 880 gas chromatograph, using a dual flame detector in conjunction with an electron capture detector. The chromatographic column was made of stainless steel 1/8 in. O. D. by 7 ft long. The column packing was 2% SE-30 (methyl silicone gum rubber) on Chromasorb Q (100-120 mesh). Operating conditions included argon carrier gas at 30 cc/min, injection block temperature 165°C, column temperature programmed from 140 to 235°C at a rate of 2°C/min. The sample volume injected was 1μl. Standardization curves for products of decomposition or reaction were prepared so that quantitative reduction of the gas chromatographic data could be achieved.

The gas chromatographic retention times were obtained for a number of possible degradation products as an aid in identifying the materials obtained on reductive decomposition of DDT. The results of these measurements follow:

Material	Source	Retention Time, min
1, 1-diphenylethane	Synthesized	1. 7
1, 1-diphenylethylene	Aldrich	1. 9
1, 2-diphenylethane	Aldrich	2. 0
trans-stilbene	Aldrich	4. 0
bis(p-chlorophenyl)methane	Eastman	5. 7

Material	Source	Retention Time, min
bis(p-chlorophenyl)ethane	Synthesized	7.8
4, 4'-dichlorobenzophenone (DBP)	Eastman	9.8
4, 4'-dichlorobenzhydrol	Pfaltz & Bauer	11.3
o, p'-DDMS	Synthesized	12.0
1, 1-bis(p-chlorophenyl)-2-chloroethylene (DDMU) or (TDEE)	Synthesized	13.0
o, p'-DDE	Aldrich	13.5
2, 2-bis(p-chlorophenyl)-1-chloroethane (p, p'-DDMS)	Isolated from DDT reduction	14.0
trans-4, 4'-dichlorostilbene (DCSt)	Synthesized	14.2
p, p'-DDE	Aldrich	15.6
o, p'-DDD	Aldrich	15.9
m, p'-DDD	Aldrich	17.1
p, p'-DDD	Aldrich	17.8
o, p'-DDT	Aldrich	18.1
p, p'-DDT	Eastman recryst.	21.0
1, 1-bis(p-chlorophenyl)-2, 2, 2-trichloroethanol-1 (Kelthane)	Rohm & Haas, recryst.	24.4
1, 1, 2, 2-tetraphenylethane	Pfaltz & Bauer	26.3
tetraphenylethylene	Aldrich	26.5
p-chlorobenzoic acid	Eastman	not observed in 47 min.
1, 1, 4, 4-tetra(p-chlorophenyl)-2, 2, 3, 3-tetrachlorobutane	Isolated from DDT reduction	not observed in 60 min.
DDA	Aldrich	not observed in 60 min.

Product Isolation Using Thin-Layer Chromatography

Good results were obtained by a technique involving thin-layer chromatography of the degradation samples, physical separation of the bands, elution of the sample from the chromatography support onto KBr discs, and analysis by infrared spectrometry.

The technique employed either Al_2O_3 or Kieselguhr plates (with added $AgNO_3$), using a 250μ thick coating on 2 x 7-7/8 in. glass plates. In one test, $30\mu l$ of a sample employing 29.1% $AlCl_3$ catalyst was placed on a Kieselguhr plate and the bands developed with n-heptane solvent. A total of 15 bands were formed. These bands were then scraped from the chromatoplate and placed in small glass capillary tubes. Approximately 1 ml of acetone was then used to elute material from the Kieselguhr onto KBr powder. The KBr was then vacuum dried to remove the solvent, formed into a disc and examined in a Beckman IR-5 spectrometer, using micro-optics. Two major products were identified from these samples. In one, strong bands assigned to p-phenyl groups, halogens, and the $\overset{|}{\underset{|}{C}}-CH_3$ grouping suggest the presence of bis(p-chlorophenyl)ethane. In another, the bands for the carboxyl group, the p-phenyl grouping and halogens indicate the presence of DDA.

In other tests samples, in which the protonated montmorillonite and the acid-form ion exchange resin were used as decomposition catalysts, were examined. In both cases, strong DDT bands and weak DDE bands were obtained by the thin-layer chromatographic method, in agreement with the gas chromatographic results.

Additional studies were conducted by the thin-layer chromatography technique in an effort to characterize the products of the zinc reduction of DDT. Analyses of samples of DDT reduced with the $Zn-(NH_4)_2SO_4$ - 96% ethanol system showed three significant bands, with R_F values of 0.65, 0.42 and 0.28. These three bands were separated, and the material was eluted from the alumina substrate with cyclohexane and analyzed by uv spectrometry.

The uv spectra strongly suggested that the first band (R_F 0.65) was bis(chlorophenyl)ethane (DDEt), the second peak was tentatively identified as 2,2-bis(p-chlorophenyl)-1-chloroethane (DDMS), and the R_F 0.28 band appeared to be DDD. These observations would tend to confirm the postulated consecutive reaction system DDT⟶DDD⟶DDMS ⟶DDEt, where the three aliphatic chlorines in DDT are reduced stepwise.

Isolation and Identification of Reaction Products

A significant study was made with the products from a reaction in which 5 g of DDT was reduced with Zn (5 g) in refluxing $(NH_4)_2SO_4$ - 95% ethanol. The reaction was carried out for 8 hrs.

When a portion of the sample was evaporated to dryness, extracted with benzene to remove inorganic salts, and crystallized from pentane, small needle-like crystals were observed (on the side of the dish) which had a melting point of about 45-50°C (the crystals were wet with an oil which made a precise melting point difficult). A sample of the fine crystals was prepared in a KBr pellet for infra-red analysis which yielded the following significant bands:

Wave Number, λ^{-1}	Assignment	Band Strength
3000	$-CH_3$	weak
2900	$-CH_2$	weak
1750		weak
1670	para-phenyl	weak
1480		strong
1085	$-\overset{\vert}{\underset{\vert}{C}} - CH_3$	strong
1010		
820	di-substituted aromatic and C-Cl bonding	medium
805		
766		medium

The spectra suggested bis(p-chlorophenyl)ethane was the product.

A sample of bis(p-chlorophenyl)ethane was prepared, therefore, for comparison. It was prepared by the method of Geigy (Reference 56). A mixture of chlorobenzene and aluminum chloride was saturated with HCl gas and reacted with acetaldehyde at -10°C. The material was then steam distilled to remove the excess chlorobenzene, the residue was dissolved in ether and the product distilled. The infrared spectra of this material appeared to match the spectra of the crystals taken from the DDT-Zn reduction reaction mix. Hence, it may be concluded that bis(p-chlorophenyl)ethane appears to be a product of the reductive degradation of DDT.

Ultraviolet spectra of the prepared bis(p-chlorophenyl)ethane and the crystals from the reaction mix also agreed. The spectra were also in agreement with those published by Keller, et al, for bis(p-chlorophenyl) ethane (Reference 57).

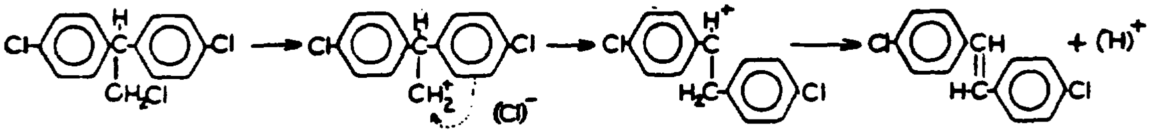
Since DDEt is an important product of the reductive degradation of DDT, it was important to establish the solubility of the material in evaluating its disposal in a waste treatment process.

Solubility estimates were made by shaking crystals of the material in water (double-distilled water), then removing excess DDEt by centrifuging at 44000 xg for 2 hr. A gas chromatographic analysis of the water indicated solubility may be as high as 10 mg/l (ppm).

Further treatment of the crystalline mass from the DDT-Zn reduction reaction mix with Freon 113 was found to dissolve the body of crystals and on cooling, crystals melting at 175°C were obtained. The Beilstein test indicated that some chlorine was present in the material.

An examination of the literature indicates the possible identity of this material. Forrest, Stephenson and Waters (Reference 58) found that DDT boiled in ethanol solution with zinc and concentrated HCl yielded three products, DDD, bis(p-chlorophenyl)ethane, and 4,4'-dichlorostilbene. The listed melting point of the dichlorostilbene is 174-178°, in good agreement with the melting point obtained for this material (175°C). It was further found that the material discolored bromine, in agreement with the results of Forrest, et al, yielding crystals with a melting point of 226°; Forrest reported a melting point of 229° for the dibromo-dichlorostilbene, in reasonable agreement with the value obtained. It was concluded that 4,4'-dichlorostilbene is a reaction product of the zinc reduction of DDT.

Forrest, et al, suggest a degradation route for DDT that appears to be compatible with observed results. Dehalogenation of the DDT to produce DDD and 1-chloro-2,2-bis(p-chlorophenyl)ethane would be followed by a molecular rearrangement of the following type to produce the stilbene derivative.



4, 4'-Dichlorostilbene

The reaction of DDT with Grignard reagent has been shown by Awe and Reinecke (Reference 59) to produce 4,4'-dichlorostilbene, the amount of the stilbene increasing as the amount of the organo magnesium halide increased.

The dichlorostilbene had a retention time of 14.2 min as measured by gas chromatography. This peak occurred frequently in reduced DDT samples, especially when reaction was forced by heating. However, other data suggested that DDMS, the monochloroethane derivative of DDT, had a similar retention time.

Additional studies were made in an effort to define the composition of the 14 min gas chromatographic peak.

One series of tests was made with the products of a zinc-DDT reaction after 21 days at 25°C. The sample contained 46.7% of a material having a 14 min retention time. The solvent was evaporated and the inorganic salts separated with Freon 113. An attempted crystallization from pentane yielded about 1% of a crystalline product with a melting point of 180°. A mixed melting point with authentic trans 4,4'-dichlorostilbene gave no melting point depression.

The oil remaining (0.615 g from reaction of 1 g DDT) was transferred to a micro still and several fractions were separated for attempted crystallization. Gas chromatographic analyses were made on the separate fractions.

Still conditions:

Bath temperature, °C	115-120	115-120	118-121
Pressure, mm	0.06-0.07	.065	.07

Gas chromatographic analyses:

DDEt, %	59.3	29.9	8.2
14 min peak, %	28.9	→ 51.7	63.1

Although enrichment was shown on distillation, crystallization experiments did not yield the pure 14 min product.

Tests were also conducted with a series of "forced" reactions. In the first set, DDT, DDD and DDE were reacted with zinc-acetone-acetic acid at reflux temperature (62°C) for 24 hours. The analyses of the products obtained from these reactions follow:

Component	Retention Time, min	Analysis, %, after Reaction for 24 hr at 62°C		
		DDT	DDD	DDE
	6.8	4.1	0.1	-
DDEt	7.8	45.2	30.2	-
	12.0	0.2	0.2	-
DDMU	13.0	4.5	-	1.9
DDMS	14.0	43.3	68.3	-
DDE	15.6	-	-	98.1
DDD	17.8	2.7	1.2	-
DDT	21.0	-	-	-

The reaction mix from the DDD reduction was evaporated and the inorganic salts separated by means of Freon 113. Concentration then gave 0.17 g of 4,4'-dichlorostilbene and 3.45 g of a colorless oil. The oil was fractionated into three fractions. A 1.37 g fraction having an approximate boiling point of 140-143°C at 0.1 mm pressure yielded crystals which on gas chromatographic analysis were shown to contain 92.9% of the 14-min peak material. The crude material was crystallized from cold hexane to give a product having 95% 14 min peak. The melting point was 49-50° (corrected). Elemental analysis yielded the following values:

Calcd. for DCSt, $C_{14}H_{10}Cl_2$:	% C = 67.48	% H = 4.02	% Cl = 28.51
Calcd. for DDMS, $C_{14}H_{11}Cl_3$:	% C = 58.88	% H = 3.88	% Cl = 37.24
Found:	57.3	3.54	35.5
	58.3	3.56	
	58.9	3.72	

Therefore, the 14 min peak was assigned to the mono-chloroethane derivative, DDMS.

Synthesis of Postulated DDT Reduction Products

1,1-Diphenylethane was synthesized from styrene and benzene by the method of Spilker and Schade (Reference 60).

1,1-Bis-(p-chlorophenyl)-2-chloroethylene (TDEE or DDMU) was prepared by the alkaline hydrolysis of DDD using the method of Haller, et al, (Reference 61).

The establishment of 2,2-bis(p-chlorophenyl)-1-chloroethane (DDMS) as a reaction product would be aided by a comparison with the spectral and chromatographic behavior of authentic material. Accordingly, an effort was made to synthesize a small amount of this material.

Hamada, et al (Reference 62) have described the condensation of chlorobenzene with chloroacetaldehyde in the presence of concentrated sulfuric acid to produce DDMS. Their procedure was modified to correspond with conditions that were found by Mosher (Reference 63) to give maximum yields of DDT.

Chloroacetaldehyde (0.1 mole) plus chlorobenzene (0.44 mole) was mixed with 220 g 98% H_2SO_4 at 4°C. Additional acid (220 g of 101% H_2SO_4) was added over a period of 4 hrs with stirring while maintaining the temperature below 5°C. The reaction was carried out in a 500 ml round-bottomed flask having four indentations that served as baffles to increase turbulence. Stirring was continued for an additional 4 hrs at 4°C and the product was extracted with four 100 ml portions of hexane at 50°C.

The hexane solution was washed with 4% Na_2CO_3, followed by water, and the hexane was allowed to evaporate in an air stream. A four gram portion of the oily residue (16 g) was distilled using a short-path micro still. The bulk of the material distilled in the range 140-150°C/0.1 mm Hg. Gas chromatography indicated a mixture of two materials with retention times of about 12 and 14 minutes. Further analysis shows that the 14 min peak is 2-chloro-1, 1-bis(4-chlorophenyl)ethane and the 12 min peak is the corresponding ortho-para isomer: 1-(2-chlorophenyl)-1-(4-chlorophenyl)-2-chloroethane.

The chloroacetaldehyde used in this reaction was prepared by chlorination of acetaldehyde at 16-18°C using 0.4 mol Cl_2 per mol of aldehyde (Reference 69). The resulting product was fractionated and material boiling in the range 80-85°C/750 mm Hg was used for condensation with chlorobenzene.

BIBLIOGRAPHIC: Aerojet-General Corp., Investigation of Means for Controlled Self-Destruction of Pesticides, Final Report FWQA Contract No. 14-12-596, June, 1970, 128 pp.

ABSTRACT: Laboratory studies demonstrated the feasibility of controlled destruction of chlorinated pesticides such as DDT. The concept comprised (1) means to degrade DDT to a harmless form, and (2) methods to delay the reaction for given pest-control action.

Chemical methods for degrading DDT were screened and reduction was selected as the most promising technique. Destruction of DDT, without forming DDE as a product, was demonstrated by mildly acidic reduction with zinc powder. The principal product is bis(p-chlorophenyl)ethane, DDT with all three aliphatic chlorines removed; a material stated to be "void of the neurotoxic effects of DDT." Catalysis of the reaction resulted in complete destruction of DDT in 1 hr at 25°C and conversion to bis(chlorophenyl)ethane in 4-8 hrs. Catalyzed aluminum or iron reduction of DDT produced tetra(p-chlorophenyl)tetrachlorobutane, reportedly lipoid insoluble.

A 90-95% destruction of DDT in soil in 4 days was demonstrated with spray-applied, integral, catalyzed zinc-DDT particles (5-micron).

Reaction delay can be achieved with wax or silicone reductant coatings which are slowly dissolved or eroded, or possibly slow air oxidation of sulfur. Coatings were produced which stopped zinc-acid reaction. A test of combined reductant - delayed action technique was made using

(over)

ACCESSION NO.

KEY WORDS:

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Reduction

Encapsulation

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Effective reductive degradation of chlorinated pesticides dieldrin, endrin, aldrin, chlordane, toxaphene, Kelthane, methoxychlor, Perthane and lindane, and selected polychlorinated biphenyls was shown.

Degradation of DDT in water was demonstrated, a 421 mg/l DDT suspension being reduced to 1 ppm after 1 hr reaction at 75°C.

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