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OF PESTICIDES AND HERBICIDES - A REVIEW

BY

W. H. DENNIS, JR.

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U.S. ARMY
MEDICAL ENVIRONMENTAL
ENGINEERING RESEARCH UNIT
EDGEWOOD ARSENAL, MARYLAND 21010



UNITED STATES ARMY

MEDICAL RESEARCH AND DEVELOPMENT COMMAND

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ABSTRACT

Degradation of pesticides, herbicides and structurally related compounds by dechlorination, photochemical reactions, cleavage of ethers, oxidation, biodegradation and hydrolysis are reviewed. Due to the great variation in chemical structure, reactivity and solubility, no single method of chemical degradation is presently available. Four approaches to chemical degradation are proposed for the detoxification of the entire spectrum of pesticides and herbicides. The methods proposed are hydrolysis, dechlorination, photolysis and oxidation. Recommendations are made for the study and development of the proposed degradative methods.

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INTRODUCTION

A number of approaches to pesticide and herbicide disposal are available; land burial, incineration or thermal degradation, or chemical, biochemical and photolytic degradation. The method used will be dependent upon the quantity of material to be destroyed, the medium in which it is dissolved or dispersed and the chemical nature of the pesticide or herbicide. Miller (1972)¹ has defined the problem of pesticide and herbicide disposal as it applies to the Department of the Army and summarized the literature dealing with thermal degradation, ground deposition (biodegradation) and some methods of chemical treatment.

The value of a chemical method for pesticide degradation lies in the destruction of small quantities of pesticides and herbicides, such as the residual material in empty containers or the excess material generated from spraying operations. Unlike land disposal which involves many parameters that control degradation, and where the half-life of the pesticide or herbicide and products of degradation would be uncertain, chemical degradation offers a predictable half-life and definite products.

The following table (Table 1) lists those pesticides and herbicides and their structural formulae which pose significant disposal problems to the Department of the Army. All research on degradation and detoxification will be conducted on these materials in both pure and commercial grades.

OBJECTIVE

This literature review summarizes various chemical and photo-chemical reactions that have been applied to pesticides, herbicides and structurally related compounds. From this survey it is hoped that some effective and practical methods can be found for the detoxification of pesticides and herbicides on both a small and large scale. This background information is needed to assess potential methods of pesticide disposal, to explore modifications of known reactions and to generate new approaches to chemical degradations of pesticides and herbicides.

TABLE 1. The Pesticides and Herbicides that Pose Significant Disposal Problems

Pesticide	Structural Formula	Military Formulation*
DDT		5% OS 25% WP 25% EC
Lindane		12% EC 1% D
Dieldrin		18% EC
Chlordane		72% EC 5% D
2,4-D and esters		Many EC and OS formulations

TABLE 1 (Cont).

Pesticide	Structural Formula	Military Formulation*
2,4,5-T and esters		Many EC and OS formulations
Malathion		95% C 57% EC
Diazinon		48% EC 2% D 0.5% OS
Propoxur		1% OS
Carbaryl		80% WP

* OS = oil solution, EC = emulsifiable concentrate, D = dust, WP = wettable powder, C = concentrate

METHODS OF CHEMICAL DEGRADATION

Chemical Dechlorination. A number of systems are described in the literature that dechlorinate both aromatic and aliphatic halides. The methods are both specific and non-specific in their actions. In general, dechlorination of a polychlorinated hydrocarbon will render it less active as a pesticide, but the degradation products may or may not be potential environmental contaminants.

The alkaline dehydrochlorination of DDT (1) to DDE (2) by alkaline substances was studied by Lord (1948)².

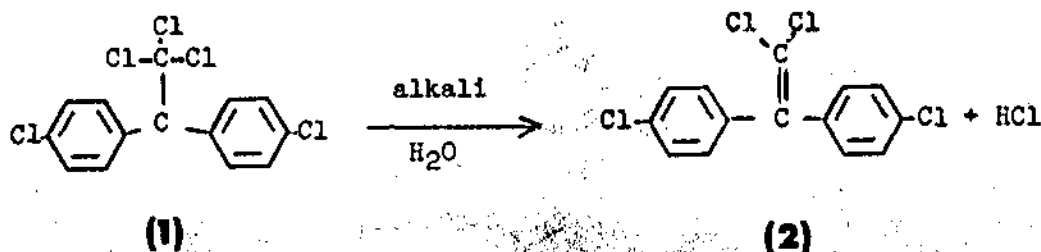


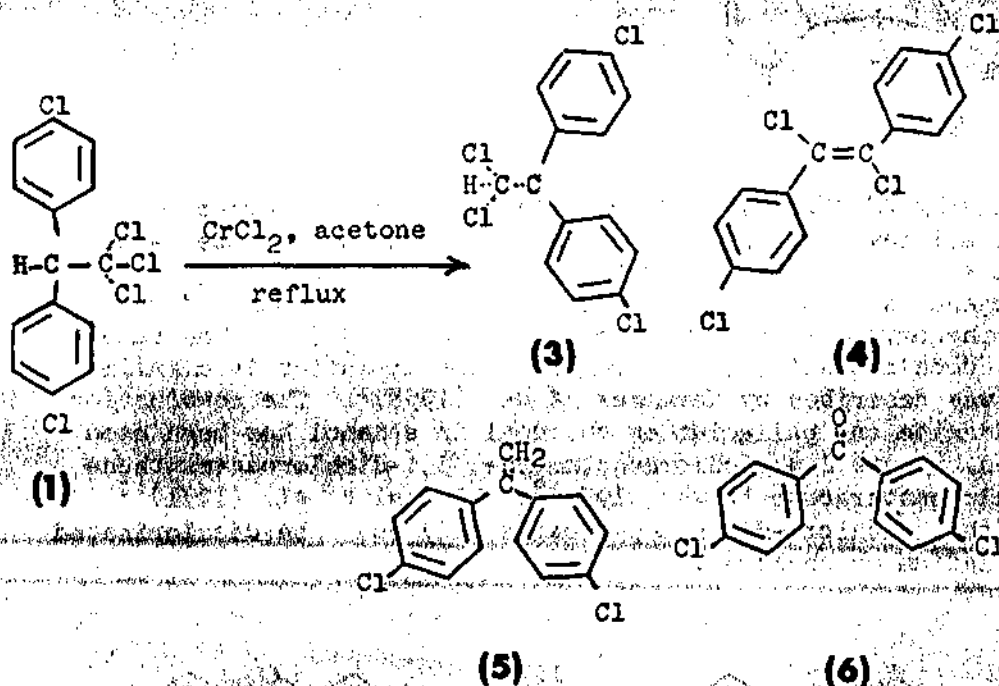
Table 2 shows the percent conversion of DDT to DDE when 1 ml of an 8% aqueous sodium hydroxide solution is added to 5 ml of 0.1 molar DDT at 30°C in an organic solvent.

TABLE 2. Conditions for Conversion of DDT to DDE (data from Lord, 1948)²

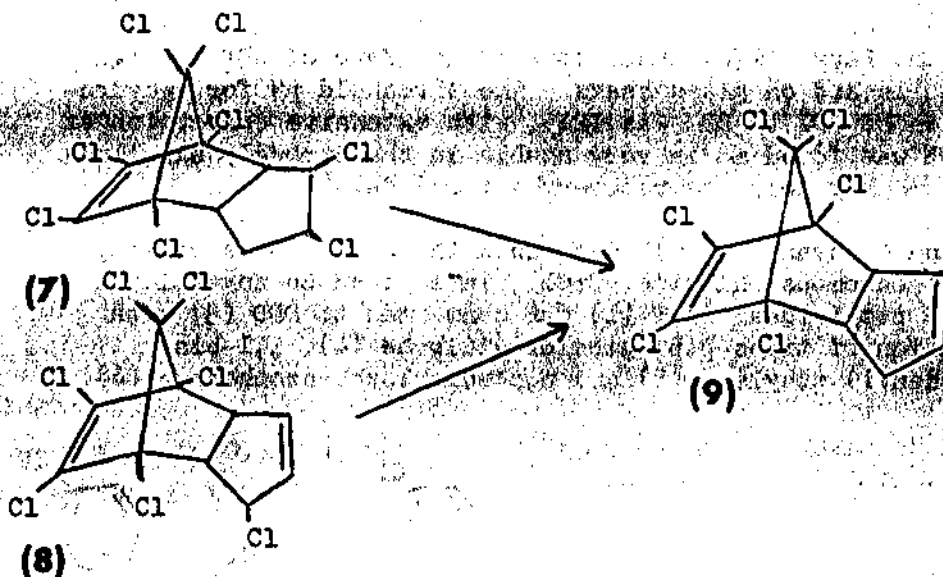
8% Aqueous NaOH	Organic Solvent (5 ml)	Reaction Time	Percent Conversion
1 ml	Benzene	25 hours	1%
1 ml	Dioxane	20 hours	45%
1 ml	Acetone	1 hour	36%
1 ml	Ethyleneglycol- monomethyl ether	1 hour	98%

Smith and Parr (1972)³ have studied the fate of DDT in highly alkaline soils and on glass beads. The threshold pH for dehydrochlorination of DDT to DDE was 12.5, with extensive conversion at pH 13. DDE was found to be very stable in the strongly alkaline media with nearly complete recovery after 7 days.

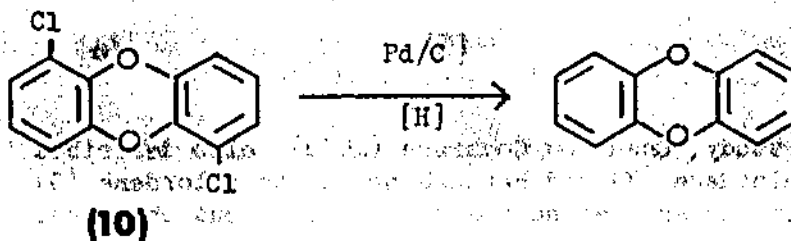
Chau and Cochrane (1970)⁴ described the action of a boiling solution of chromous chloride, CrCl_2 , in acetone on several chlorinated pesticides. DDT (1) was converted to DDD (3) with some formation of trans-p,p'-dichlorostilbene (4), 1,1-bis-(p-chlorophenyl) ethylene (5) and p,p'-dichlorobenzophenone (6).



In another study, Chau and Cochrane (1970)⁵ also described the reduction of chlordane (7) and heptachlor (8) to chlordene (9) after prolonged boiling in an acetone solution of chromous chloride.

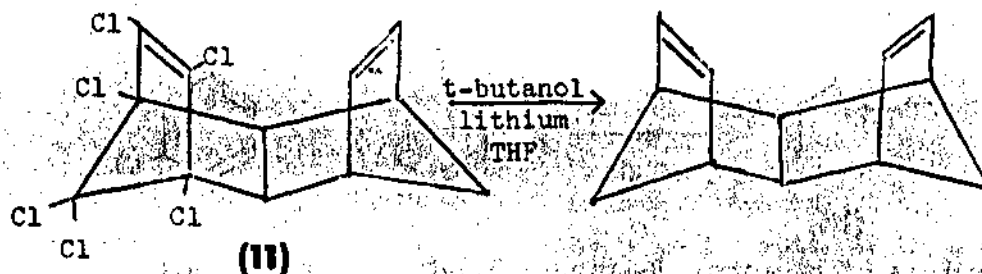


Schwenk *et al.* (1944)⁶ found that aromatic chloro-compounds quantitatively exchange halogen for hydrogen when treated with nickel aluminum alloy in aqueous alkali. Raney nickel or cobalt dehalogenates mono and dichlorobenzene, chlorophenols and p-chlorophenoxyacetic acid with ease (Buu-Hoi, 1963)⁷. The raney nickel dechlorination of chloro and bromo aromatics in alkaline media was described by Kammerer *et al.* (1958)⁸. The combination of hydrazine and palladium on charcoal in ethanol has been used to dechlorinate 1,4-dichloronaphthalene, 5,6-dichloroacenaphthene and chloroanthracene (Mosby, 1959)⁹. Vinopal *et al.* (1971)¹⁰ found that dichloro-dibenzo-p-dioxins (10) could be dechlorinated by palladium on charcoal.

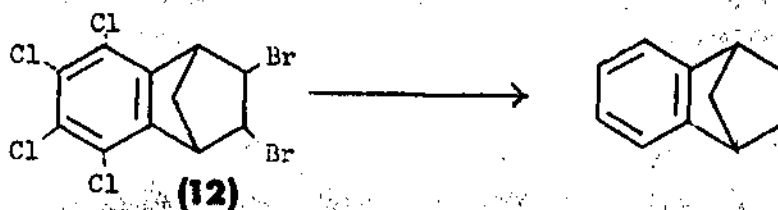


A highly active catalyst that is inexpensive is nickel boride, Ni_2B . Nickel boride is produced by the reaction of a soluble nickel salt with aqueous sodium borohydride (Brown and Brown, 1963)¹¹ (Mal'tseva *et al.*, 1967)¹². Although Ni_2B has not been applied to dechlorination, it has been applied to the hydrogenation of olefins (Brown and Brown, 1963)¹¹ and the desulfurization of thiols (Truce and Perry, 1965)¹³.

The total dechlorination of isodrin (11) was achieved by Bruck *et al.* (1960)¹⁴ using *t*-butyl alcohol and lithium metal in tetrahydrofuran (THF). Geminal, allylic and bridgehead chlorine atoms are replaced by hydrogen with ease.



Bruck (1969)¹⁵ also demonstrated the total dechlorination of 2,3-dibromo-3',4',5',6'-tetrachloro-benzonorborene (12) with the lithium-butanol-THF system.

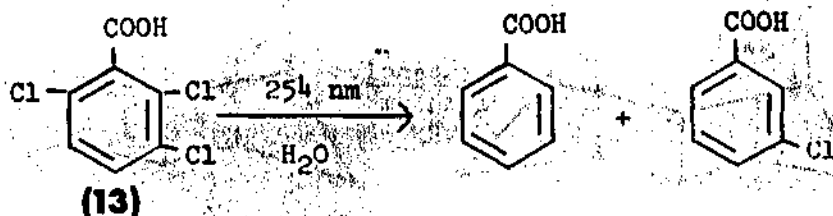


Gassmann and Pape (1964)¹⁶ showed that the same dechlorination could be obtained if sodium metal were substituted for lithium. However, it was found that the sodium-butanol-THF system also reduced olefinic bonds present in some of the polychloro compounds.

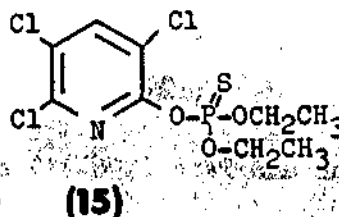
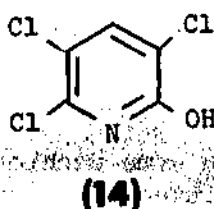
Photochemical Degradation. Photochemical reactions of halogenated aromatic compounds are free-radical in nature. Studies show that generally light from a mercury arc (254 nm) is sufficient to cause photodecomposition. Photolysis yields a chlorine atom and a phenyl radical. The fate of the phenyl radical is dependent upon the medium of the reaction. Water generally affords hydroxylated products where solvents such as alcohol and benzene undergo hydrogen abstraction.

Replacement of halogen by the hydroxyl group during photolysis of chloroaromatics is described by Plimmer (1970)¹⁷. This author

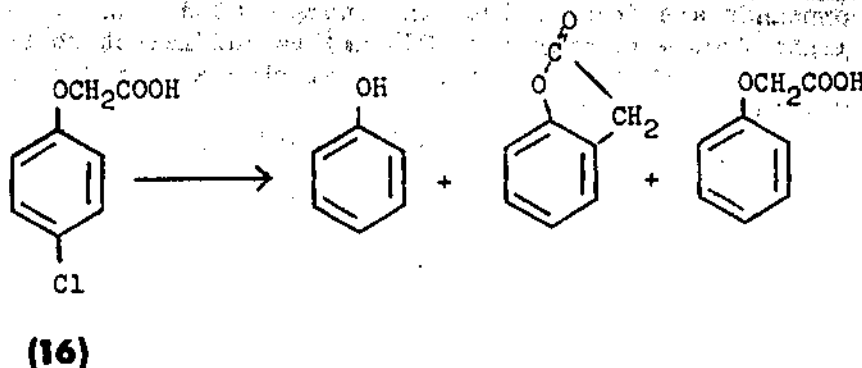
also found that the herbicide 2,3,6-trichlorobenzoic acid (13) yields benzoic acid and *m*-chlorobenzoic acid when exposed to UV light.



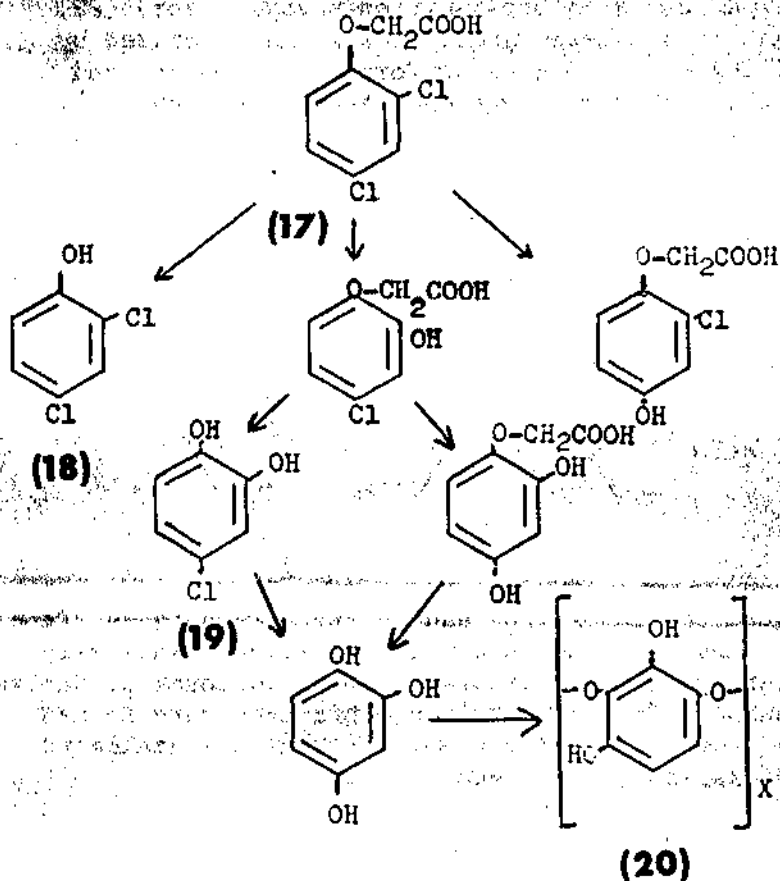
Photolysis of picloram, 4-amino-3,5,6-trichloropicolinic acid, at 254 nm yields two moles of chloride per mole of picloram (Kearney *et al.*, 1969)¹⁸. An aqueous solution of 3,5,6-trichloro-2-pyridinol (14) which is related to the pesticide chlorpyrifos (15) undergoes dehalogenation when exposed to sunlight or artificial UV light (Smith, 1968)¹⁹. Spectrophotometric measurements of (14) indicated that cleavage of the pyridine ring also occurred.



Pinhey and Rigby (1969)²⁰ showed that chlorobenzene, chlorophenol and *p*-chlorophenoxyacetic acid (16) undergo photolysis in isopropanol.

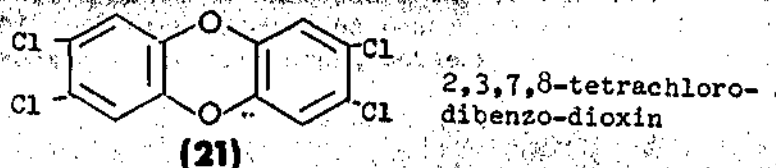


Crosby and Tutass (1968)²¹ observed the rapid decomposition of the herbicide 2,4-D (17) in water in the presence of UV light. There was a 50% loss of 2,4-D in 5 minutes at pH 7. The major reaction was the cleavage of the ether bond to produce 2,4-dichlorophenol (18) which was dehalogenated to 4-chlorocatechol (19). Ultimately, the product of extended photolysis was a mixture of polyquinoid humic acids (20).

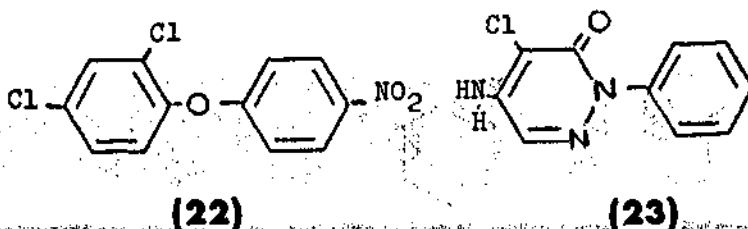


A five minute exposure of an aqueous solution, 5 ppm. of 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) to UV light destroyed its herbicidal activity (Kearney *et al.*, 1969)¹⁸. Chlorinated dibenzo-P-dioxins (21) which are powerful teratogenic agents and found as trace impurities in the herbicides 2,4-D and 2,4,5-T are decomposed

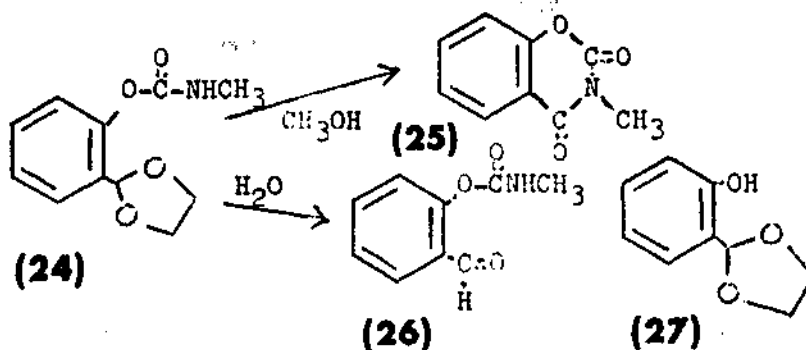
by sunlight or artificial light at 300 nm (Plimmer *et al.*, 1971)²². In methanol, the chlorine substituents are replaced by hydrogen, followed by disruption of the heterocyclic ring.



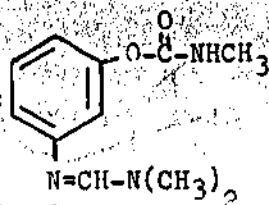
Nakagawa (1971)²³ found that an aqueous solution or suspension of the herbicide TOK (2,4-dichloro-4-nitrodiphenyl ether) (22) exposed to sunlight or simulated sunlight was characterized by rapid cleavage of the ether linkage to form *p*-nitrophenol and 2,4-dichloro-phenol. Other products were 4-chlorocatechol, 4-nitrocatechol, 4-chloro-4-nitrodiphenyl ether, 2,4-dichloro-4-amino-diphenyl ether and *p,p'*-di-(2,4-dichlorophenoxy) azobenzene. Irradiation of aqueous pyrazon (23) at 250 nm for 6 hours resulted in a mixture of ten products (Rosen, 1971)²⁴.



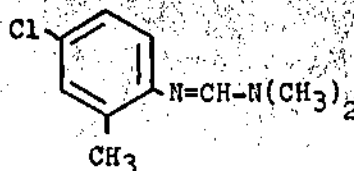
Using gas-liquid chromatography and infrared techniques, Pape *et al.* (1970)²⁵ found that the insecticide 2-(1,3-dioxalane-2-yl) phenyl-*N*-methyl carbamate (24) yielded 85% of a benzoxazine derivative (25) in methanol. In water, multiple products were formed, two of which were identified as 2-*N*-methylcarbamyl benzaldehyde (26) and 2-(1,3-dioxalane-2-yl) phenol (27).



The photolysis of the new pesticide *m*-(*N,N*-dimethylformamidine) phenyl-*N*-methyl carbamate (28) was carried out in water at pH 3.1 and 7.1 (250 ppm) using light at the wavelengths greater than 286 nm (Su and Zabik, 1972)²⁶. Four products were detected. In another study these investigators (1972)²⁷ irradiated an aqueous solution of *N'*-(4-chloro-*o*-tolyl)-*N,N*-dimethylformamidine (29) under similar conditions to form two products.

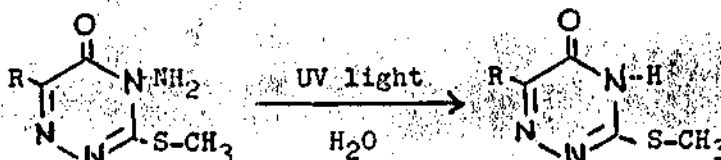


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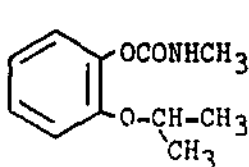
(29)

Pape and Zabik (1972)²⁸ studied the photolysis of three 4-amino-6-alkyl substituted-3-(methyl-thio)-*s*-triazin-5(4*H*)-ones (30) at wavelengths longer than 290 nm. In all cases there was loss of the amino group. These photoproducts were reportedly considerably less biologically active than their parent compounds.

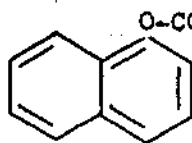


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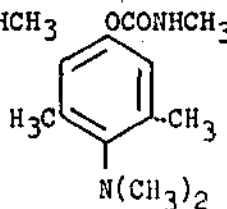
Crosby *et al.* (1965)²⁹ irradiated six *N*-methyl carbamate insecticides in ethanol using both sunlight and artificial UV light. The insecticide propoxur (31) was found to be inert to the exposure whereas the other compound which included carbaryl (32), Zectran (33) and Mesurool (34) decomposed to give unidentified cholinesterase inhibitors as well as other substances. Thin-layer chromatography (TLC) was used to analyze the reaction mixtures.



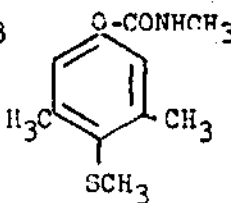
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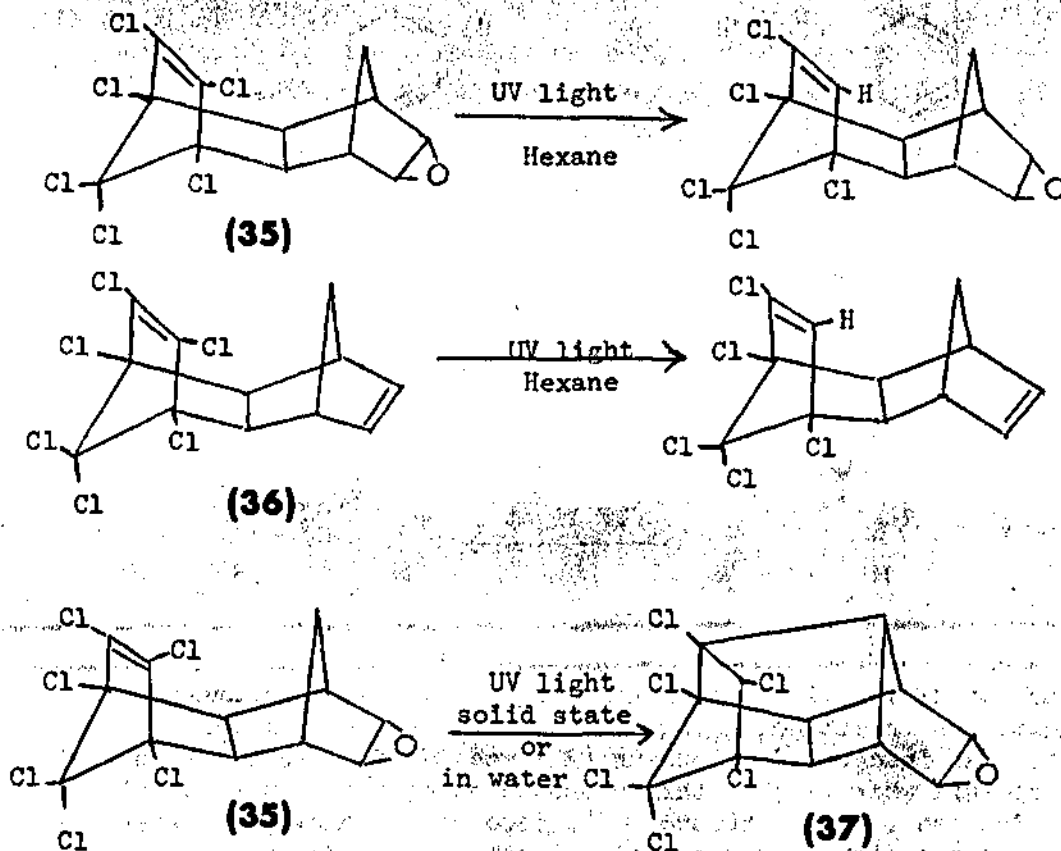


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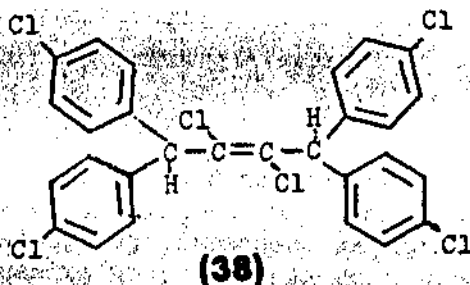


(34)

Irradiation of dieldrin (35) in hexane yields a pentachloro-derivative that is less toxic to flies, but is five times more toxic to mice. Aldrin (36) undergoes a similar mono-dechlorination (Henderson and Crosby, 1967)³⁰. In the solid phase, both dieldrin and aldrin undergo rearrangement without loss of chlorine (Cookson and Crundwell, 1958)³¹ (Robinson *et al.*, 1966)³² (Rosen and Sutherland, 1967)³³. The same photochemical product (37) is formed when a saturated aqueous solution of dieldrin is exposed to UV light (Henderson and Crosby, 1968)³⁴.

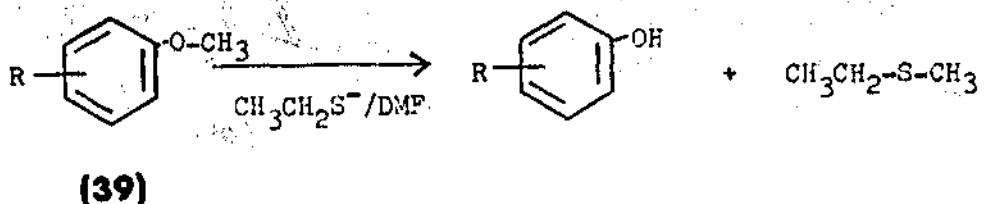


When Fleck (1949)³⁵ irradiated a solution of DDT in ethanol with a mercury vapor lamp for 16 hours, about one mole of HCl was evolved with some acetaldehyde. The product of this reaction was 1,1,4,4-tetrakis-(*p*-chlorophenyl)-2-butene (38) obtained in a 10% yield.



Kinney and Ivanuski, (1969)³⁶ have studied aqueous slurries of zinc and titanium oxides which act as photocatalysts. Irradiation of these slurries with a sunlamp resulted in the formation of atomic oxygen which could oxidize dissolved organic matter such as phenol, acetic acid, sodium stearate and sucrose. This technique was not applied to pesticides or herbicides.

Chemical Cleavage of Ethers. Another approach to the degradation of 2,4-D and 2,4,5-T is by cleavage of the ether bond by chemical means. The photo-induced cleavage of the ether bond was described earlier (Crosby and Tutass, 1968)²¹. The only description of direct cleavage of 2,4-D and 2,4,5-T is that of Marquardt (1961)³⁷ who demonstrated the formation of chlorophenols when the herbicides were fused with pyridine hydrochloride. Rapid and quantitative demethylation of aryl ethers (39) can be accomplished using sodium thioethoxide in hot dimethylformamide (DMF) (Featrill and Mirrington, 1970)³⁸.

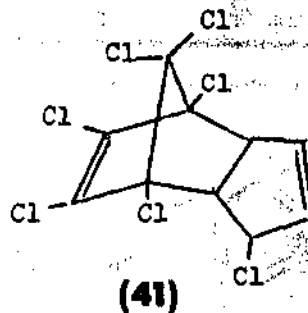
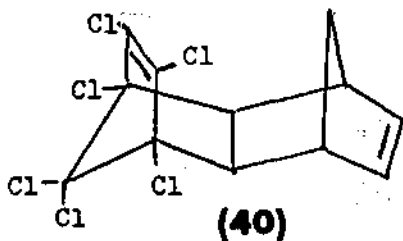


Demethylation of ethers can also be carried out by magnesium iodide in benzene-ether solution (Schonberg and Sina, 1950)³⁹ or by lithium iodide in boiling collidine (Harrison, 1969)⁴⁰.

Sodium amide in boiling piperidine cleaves diaryl or aryl-alkyl ethers and converts aryl halides to aryl piperidines (Brotherton and Bunnett, 1957)⁴¹.

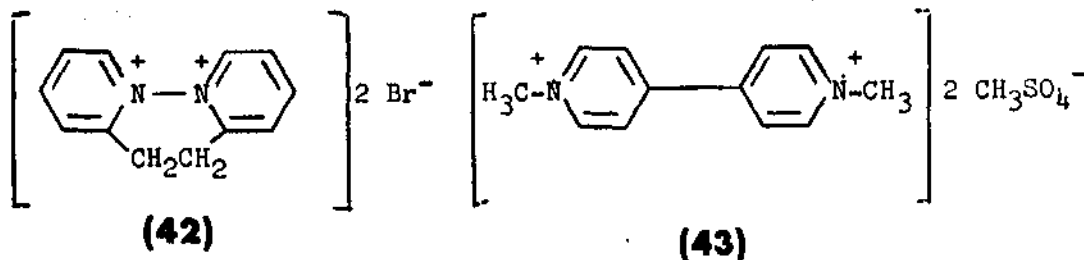
Degradation by Oxidants. Strong oxidants offer still another approach to destroying pesticides and herbicides. However, the water insolubility of many of the compounds, particularly the chlorinated pesticides, makes the use of strong oxidants in water media generally impractical.

Hydrogen peroxide is reported to react with both 2,4-D and 2,4,5-T (Iyr, 1963)⁴². Dieldrin, lindane and DDT at ppb levels in water were not removed by chlorine or permanganate and only partly removed by ozone (Robeck, 1965)⁴³. In a more recent study (Hoffman and Eichelsdoerfer, 1971)⁴⁴, the oxidation of chlorinated pesticides by ozone in both water and hexane was investigated. Of the compounds aldrin, dieldrin, heptachlor, heptachlor epoxide, chlordane, lindane, DDT and endosulfan; only aldrin (40) and heptachlor (41) reacted quantitatively. This study indicates that only compounds having unchlorinated olefinic bonds, such as aldrin and heptachlor, undergo reaction with ozone. Williamson and Cvetanovic (1968)⁴⁵ showed that ozone reacts with pentene 2,200 times more rapidly than with *cis*-dichloroethylene.



Buescher *et al.* (1964)⁴⁶ showed that potassium permanganate at 40 ppm removed aldrin and partly removed lindane from water; ozone removed aldrin, dieldrin and lindane; and hydrogen peroxide at 40 ppm had no effect on any of these three pesticides. Gomaa

and Faust (1971)⁴⁷ found that chlorine dioxide (ClO_2) oxidized the herbicides diquat (42) and paraquat (43) extremely fast in water at pH 8.14 to pH 10.15 when the concentration of the herbicides were 30 mg/l. The reaction time was 1 minute. Chlorine dioxide was unreactive at pH 5.06 to 7.12, but in the range 8.14 to 10.13 degradation of the quaternary compounds was observed. Potassium permanganate was also effective in degrading the herbicides in the alkaline pH range. The investigators made the assumption that the products of the reaction were CO_2 , oxalate ion, ammonia and water, but this was not proven by analysis.



Other oxidation systems that are non-aqueous or partly aqueous and would be compatible with the water insoluble pesticides are potassium permanganate in acetone (Smith and Rouault, 1943)⁴⁸, permanganate and periodate in *t*-butanol and water (Lemieux and von Rudloff, 1955)⁴⁹, ruthenium tetroxide and sodium periodate in acetone and water (Stork *et al.*, 1963)⁵⁰ and tetrabutylammonium permanganate in chloroform (Davis, 1972)⁵¹. Although these oxidation systems have been used on various compounds containing olefinic bonds, they have not been applied to pesticides or herbicides.

Biodegradation. Degradation of pesticides and herbicides in the aquatic or soil environment is possible by many ways; photodecomposition, biological uptake and metabolism and chemical and biological oxidation, reduction or hydrolysis. Since pesticide and herbicide residues are found in the soil and water, the natural degradation is clearly slow and unpredictable. Work has been done to understand the fate of DDT, aldrin, dieldrin and endrin in the marine environment (Patil, 1972)⁵². Faust and Goma (1972)⁵³ have pointed out that the organophosphorous and carbamate pesticides, which are

susceptible to alkaline or acid hydrolysis, are quite persistent under natural environmental condition, that is the temperature of 0° to 25°C and a pH range of 5.5 to 8.5. A recent report by Miller (1972)¹ offers a comprehensive survey of the literature dealing with microbial action on pesticides and herbicides in the soil.

Degradation by Hydrolysis. Although many of the organophosphorous and carbamate pesticides are persistent under environmental conditions of temperature and pH, see Table 3, these compounds are generally unstable in strongly alkaline or acid media.

TABLE 3. Hydrolysis Rates of Four Pesticides Under Ambient Conditions (data from Faust and Goma, 1972)⁵³

Pesticide	pH and Temp.		Half-life
Diazinon	7.4	20°C	4436 hrs (184 days)
Parathion	7.4	20°C	2594 hrs (108 days)
Thimet*	6.9	20°C	450 hrs (19 days)
Dichlorvos*	6.9	20°C	260 hrs (11 days)

*in ethanol: water = 1:4

The literature cites the hydrolyses of many pesticides under a variety of conditions. However, many of these studies are not meaningful in that high temperatures and neutral pH are used in the determination of half-lives of the compounds. Such a study is that of Ruzicka *et al.* (1967)⁵⁴ where the half-lives of 31 pesticides are reported at pH 6.9 and 70°C in an ethanol-water mixture. Extrapolation of these results to lower or higher pH is not possible. Some hydrolysis studies were found that are more useful in understanding the stability of organophosphorous

pesticides. Such a study is that of Faust and Gomaa (1972)⁵³, see Table 4.

TABLE 4. Half-Lives of Two Pesticides at 20°C and Various Conditions of pH (data from Faust and Gomaa, 1972)⁵³

Diazinon		Parathion	
pH	Half-life	pH	Half-life
3.1	12 hrs	3.1	4182 hrs
5.0	742 hrs	5.0	3670 hrs
7.4	4436 hrs	7.4	2594 hrs
9.0	3263 hrs	9.0	523 hrs
10.4	145 hrs	10.4	33 hrs

The half-lives of other organophosphorous and carbamate pesticides under alkaline conditions and ambient temperature are shown in Table 5.

The toxicity of the hydrolysis products of the organophosphorous and carbamate pesticides to mammals and fish must be considered if hydrolysis is used to dispose of a pesticide. Table 6 lists the data available for some compounds of special interest to the Department of the Army.

TABLE 5. Half-Lives of Various Pesticides Under Alkaline Conditions

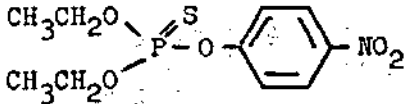
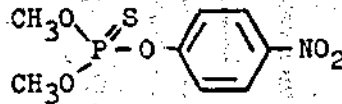
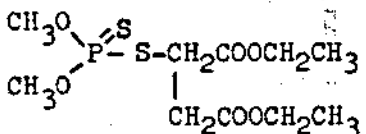
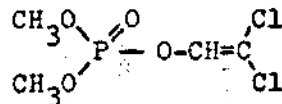
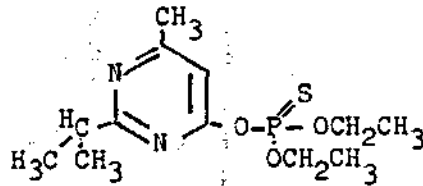
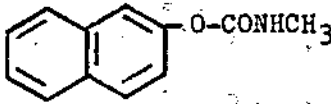
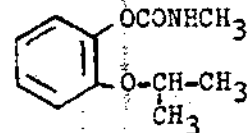
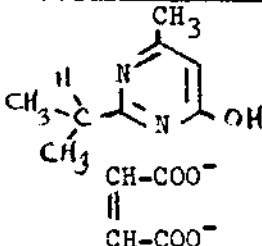
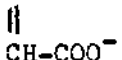

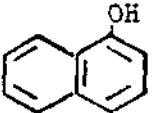
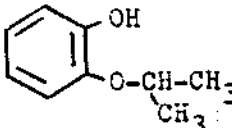
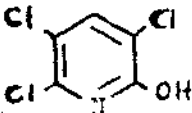
Pesticide	Structural Formula	Experimental Conditions		Half-Life	Ref.
		Temperature	pH		
Parathion		15°C	1 N NaOH	32 min.	55
Methyl parathion		15°C	1 N NaOH	7.5 min.	55
Malathion		25°C	10.03	28 min.	56
DDVP		37.5°C	8.0	462 min.	57
Diazinon		20°C	10.4	144 hrs.	53
Carbaryl		ambient	alkaline	rapid	58
Propoxur		20°C	10.0	40 min.	59

TABLE 6. Acute Toxicities of Various Pesticides and Their Alkaline Hydrolysis Products

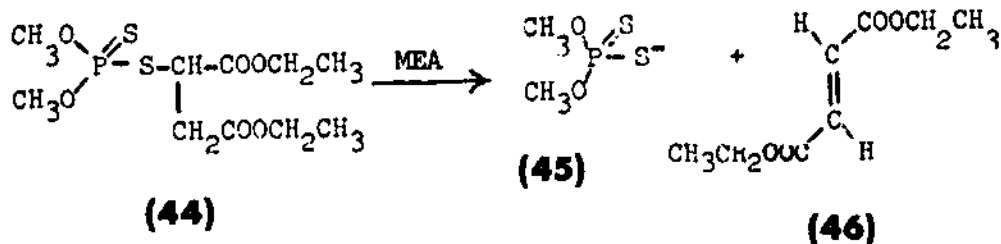
Pesticide	Pesticide Acute Toxicity (LD ₅₀)	Hydrolysis Product	Hydrolysis Product Toxicity
Diazinon	Rat (oral) 66-600 mg/kg ⁵³		LD ₅₀ - rat (oral), ⁵³ 2700 mg/kg
Malathion	Rat (oral) 480-5800 mg/kg ⁶⁰		Human dose of 500 mg/day ⁶⁴ for one year, no effect
69 Parathion	Rat (oral) 3-30 mg/kg ⁵³		Cat (sc) 197 mg/kg MLD ⁶⁵ Dog (iv) 10 mg/kg LD
Carbaryl	Rat (oral) 560 mg/kg ⁶¹		Cat (oral) 100-150 mg/kg ⁶⁵ Rabbit (oral) 9000 mg/kg LD
Propoxur	Rat (oral) 100 mg/kg ⁶²		Not known
Chlorpyrifos	Rat (oral) 163 mg/kg ⁶³		Not known

The American Cyanamid Company has published a booklet (Anonymous)⁶⁶ on the decontamination and disposal of organophosphorous pesticides (manufactured by Cyanamid) and their containers. This publication recommends the use of an aqueous caustic soda and detergent solution for rinsing empty pesticide containers followed by burial of the container and rinse solution in an isolated area. Table 7 shows the composition of the rinse solution for various container sizes.

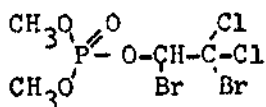
TABLE 7. Rinse Solution Mixtures for Organophosphorous Pesticide Containers of Various Sizes

Container Size	Water	Detergent	Caustic Soda
5 gal	1/2 qt.	1 tblsp.	1/4 lb.
5 gal.	2 qt.	1/4 cup	1/4 lb.
15 gal.	1.5 gal.	1/4 cup	1/2 lb.
30 gal.	3 gal.	1/2 cup	1 lb.
55 gal.	5 gal.	1 cup	2 lb.

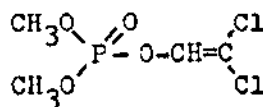
Richter (1971)⁶⁷ studied the mechanism by which 2-aminoethanol (monoethanolamine, MEA) in a polar, nonaqueous solvent such as dipropyleneglycol monomethyl ether (DPGME) decontaminates malathion (44). The main reaction products were 0,0-dimethyl dithiophosphate (45), and diethylfumarate (46). The latter compound underwent addition by a molecule of MEA.



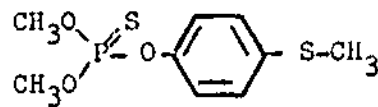
Wolverton *et al.* (1971)⁶⁸ used 12.5% and 25% solutions of monoethanolamine, MEA, in dipropylene glycol monomethylether (DPGME) to decontaminate the insecticides malathion (44), naled (47), dichlorvos (48), fenthion (49) and TEPP (50). Ten parts of decontaminant solution was used to one part of insecticide, and the disappearance of the insecticides monitored by GLC and TLC. Dichlorvos, naled and TEPP were completely destroyed in 30 minutes by hydrolysis; malathion was gone in 120 minutes and about 50% of the fenthion remained unreacted after 240 minutes at room temperature. The mixture of MEA and DPGME was found to be relatively non-toxic to the mosquito fish (*Gambusia affinis*). These fish could tolerate MEA and DPGME at levels of 330 ppm and 8000 ppm respectively. Fish exposed to the decontaminant mixture containing malathion or naled tolerated 2073 ppm for the degraded naled mixture (96 hour exposure).



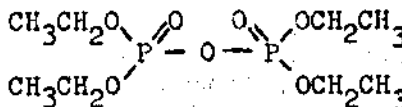
(47)



(48)



(49)



(50)

The use of MEA in decontamination of the irritant CS (o-chloro-benzylidene malononitrile) was described by Demek *et al.*, (1968)⁶⁹. This study showed that 10% MEA in water containing 0.3% of a nonionic detergent would dissolve and rapidly hydrolyze the CS. It is possible that an aqueous MEA solution may dissolve the pesticides as well.

CONCLUSIONS

No single chemical procedure for degrading the entire spectrum of pesticides and herbicides exists. Due to the great variation in

chemical structures and solubilities, several approaches to degradation will be needed. It is probable that with three or four diverse chemical methods, any compound can be effectively detoxified. From the known reactions of pesticides and herbicides, four general methods can be set down:

1. Hydrolysis. Hydrolysis proves to be the most practical and reliable method of destroying organophosphorous and carbamate pesticides. The MEA - dipropylene glycol monomethyl ether system described by Wolverton *et al.*, (1971)⁶⁸ shows great utility toward the destruction of organophosphorous pesticides. The system is relatively non-toxic and non-corrosive, and being a homogeneous system, allows the determination of the half-life of the compound to be hydrolyzed. It is possible that an aqueous MEA solution will dissolve the pesticides as well. From the standpoint of a fire hazard, an aqueous solution would be more desirable. An investigation of systems using MEA in a partly aqueous medium should be carried out to determine the reaction rates of both organophosphorous and carbamate insecticides that are of interest to the Department of the Army.

2. Dechlorination. The polychlorinated pesticides can be best degraded by chemical dechlorination. The system using *t*-butyl alcohol, tetrahydrofuran and lithium or sodium metals should be the most effective and non-specific in dechlorination. The disadvantage of this system lies in the fire hazard created by the hydrogen produced from the reaction of an alkali metal with the alcohol, and the use of tetrahydrofuran (an ether). A catalytic system shows promise in dechlorination of the polychlorinated compounds. An inexpensive catalyst worth investigating is nickel boride. The simplicity of its preparation, and its high activity as a catalyst, makes it an excellent candidate for research.

3. Photolysis. The photolytic approach to decontamination seems to be a practical method that merits investigation. This approach is particularly useful in degrading 2,4-D and 2,4,5-T as well as the chlorodibenzodioxin impurities. In the cases where a pesticide is dissolved in oil, such as diazinon, photolytic decomposition may be a better approach than using an emulsifying hydrolytic medium. Experimental work needs to be done to determine the rates of degradation of pesticides and herbicides in both sunlight and UV light, and assessing the toxicity of the photo-products.

4. Oxidation. Chemical oxidation is a fourth approach to pesticide and herbicide decontamination that is worth study. The reaction of chlorine dioxide with water-soluble compounds like 2,4-D and 2,4,5-T has not been investigated. Oxidations of pesticides carried out in non-aqueous or partly aqueous solutions are also poorly understood.

Each of these procedures would encompass a large number of pesticides and herbicides that would be effectively detoxified. The development of each system should be carried out with the following two guidelines:

1. Reagents and solvents should be:
 - a. Relatively common
 - b. Low in cost
 - c. Produce no fire hazard
 - d. Non-toxic to fish and mammals
2. The medium in which the reaction is carried out should be compatible with both water soluble and water insoluble compounds.

RECOMMENDATIONS FOR FUTURE STUDY

1. Hydrolysis Studies.

a. Find hydrolytic systems compatible with the pesticides of main interest to the Department of the Army (DA).

b. Determine the hydrolysis rates of the organophosphorous and carbamate pesticides in one or more systems.

c. Determine the nature of the products from the hydrolyses and assess their toxicity.

2. Photolytic Studies.

a. Determine the rate of photolysis of 2,4-D and 2,4,5-T

and their esters in water and alcohol using artificial and natural light.

b. Investigate photolysis of pesticides and herbicides of interest to DA, determine their reaction rates and the toxicity of photoproducts.

c. Investigate photosensitizing chemicals to promote more rapid and efficient photochemical reactions.

3. Dechlorination Studies.

a. Investigate suspensions of nickel boride, Ni_2B , as a dechlorinating agent and determine reaction rates if successful.

b. Modify the lithium-THF-*t*-butanol system for dehalogenation to make it safer and more practical.

4. Oxidation Studies.

a. Investigate a number of organic oxidation systems with various pesticides.

b. Study the reaction of aqueous chlorine dioxide with 2,4-D, 2,4,5-T and other pesticides and herbicides.

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<p>Degradation of pesticides, herbicides and structurally related compounds by dechlorination, photochemical reactions, cleavage of ethers, oxidation, biodegradation and hydrolysis are reviewed. Due to the great variation in chemical structure, reactivity and solubility, no single method of chemical degradation is presently available. Four approaches to chemical degradation are proposed for the detoxification of the entire spectrum of pesticides and herbicides. The methods proposed are hydrolysis, dechlorination, photolysis and oxidation. Recommendations are made for the study and development of the proposed degradative methods.</p>			

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