Table IX. Comparison of the Aldicarb Carbamate Residues Found in Cottonseed and Foliage by the Radiometric and Residue Analysis Procedures

Residue	Cottonseed		Cotton foliage			
			Radiometric method		Residue method	
	Radiometric method	Residue method	Sample 1	Sample 2	Sample 1	Sample 2
Aldicarb	ND[a]	—[b]	Trace	Trace	<0.01	0.06
Aldicarb sulfoxide	0.08	—	0.4	8.7	0.27	8.7
Aldicarb sulfone	0.21	—	0.6	13.3	0.69	14.1
Total toxic residue	0.29	0.23	1.0	22.0	0.96	22.9

[a] ND, none detected. [b] A dash signifies the particular residue was not separately determined.

(Table VIII) and by analysis of seed from plants treated with radioactive aldicarb and thus containing grown-in radioactive residues. Comparative results from radiometric and residue analyses of these seeds, as well as foliage from the plants, are seen in Table IX. These data prove the applicability of the residue methods to cotton seed and foliage, as have corollary exhaustive extraction tests on cottonseed, which show 98% of the seed residue is extracted in two extractions as stipulated in the residue method.

The determination limit of the residue method is about 0.01 ppm. Typically, untreated control samples show little variation in the base line near the retention time of the pesticide (Figure 1). One peak, eluting with a retention time of about 4 min, is seen in varying quantities in cottonseed as well as other agricultural and environmental substrates. No serious attempt has been made to identify this peak, since it does not interfere in the determinations.

ACKNOWLEDGMENTS

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Photodecomposition of the Herbicide Methazole

G. Wayne Ivie,[1] H. Wyman Dorough,* and Raymond A. Cardona

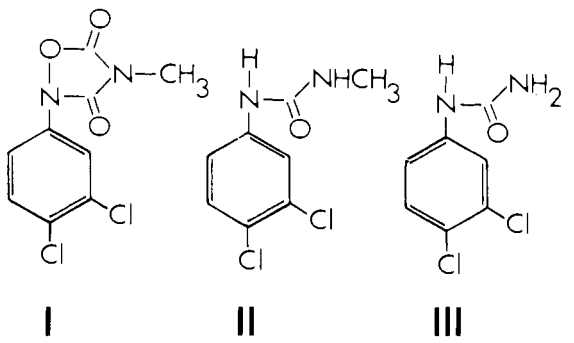
Exposure of methazole [2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione] to ultraviolet light in methanol or to sunlight in water or as surface deposits resulted in loss of carbon dioxide from the oxadiazolidine ring with subsequent generation of several derivatives. Photoproducts identified include 3,4-dichloronitrobenzene, 1-(3,4-dichlorophenyl)-3-methylurea, 1-(3,4-dichlorophenyl)urea, and two isomeric dichloro-1-methyl-2-benzimidazolinones. The methylurea and urea compounds were not produced in methanol, but 1-(3,4-dichlorophenyl)-3-methoxymethylurea was generated in rather large quantities. This compound degraded to the urea during workup of the photolysis mixture. The two isomeric dichloro-1-methyl-2-benzimidazolinone photoproducts were not phytotoxic to bean or tomato foliage, but were more toxic to mice than methazole when administered ip.

Methazole [Probe, bioxone, VCS-438, 2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione] (I) is an experimental herbicide currently under development by Velsicol Chemical Corp. This compound has shown excellent potential for control of selected weed species in several crops, particularly cotton.

In studies of methazole metabolism by cotton plants, 1-(3,4-dichlorophenyl)-3-methylurea (II) and 1-(3,4-dichlorophenyl)urea (III) were identified as the major metabolites, while several other unidentified products also were observed (Jones, 1971; Jones and Foy, 1972). Metabolites

Department of Entomology, University of Kentucky, Lexington, Kentucky 40506.
[1] Present address: Veterinary Toxicology and Entomology Research Laboratory, Agricultural Research Service, United States Department of Agriculture, College Station, Texas 77840.

II and III are generated by opening of the methazole (I) heterocyclic ring with concurrent loss of carbon dioxide to form the methylurea, and then demethylation to the urea.



I II III

Limited studies on the photodegradation of methazole were conducted by observing its decomposition when surface deposits were held in an environmental chamber. At least five major degradation products were detected, two of which chromatographed on single-dimension thin-layer chromatography (tlc) with authentic II and III. The nature of the remaining photoproducts was not investigated (Jones, 1971).

The studies reported here were undertaken to more thoroughly define the photochemical pathways of methazole, and to determine the toxicity of major photoproducts which may occur in the environment subsequent to the use of this compound.

MATERIALS AND METHODS

Chemicals. Samples of methazole and certain of its analogs considered as possible photoproducts were supplied by Velsicol Chemical Corp., Chicago, Ill. Three radiocarbon-labeled methazole preparations used in these studies were also supplied by Velsicol. These included: methazole-phenyl-^{14}C (13.50 mCi/mmol); methazole-3-carbonyl-^{14}C (7.66 mCi/mmol); and methazole-5-carbonyl-^{14}C (15.72 mCi/mmol). The phenyl and 3-carbonyl labels were purified on tlc to >98% radiochemical purity. The 5-carbonyl label did not require additional purification. Prior to use, the specific activity of each preparation was adjusted to 33,000 dpm/μg by dilution with unlabeled methazole.

Analytical Procedures. Infrared (ir) spectra were recorded as 2% potassium bromide pellets on a Beckman IR-4 spectrophotometer. Mass spectra (ms) were determined on a Hitachi RMU-7 instrument, and proton magnetic resonance (pmr) spectra were recorded as 10% solutions in dimethylsulfoxide-d_6 or acetone-d_6 on a Varian T-60 spectrometer with tetramethylsilane as an internal reference. Elemental analyses were performed in the laboratories of Velsicol Chemical Corp., Chicago, Ill. Melting points were determined in open capillary tubes with an electrothermal melting point apparatus.

Tlc was accomplished using silica gel F_{254} precoated chromatoplates (0.25-mm gel thickness, Merck AG, Darmstadt, Germany), with routine development in petroleum ether–chloroform–ethanol (7:2:1). Visualization was afforded by radioautography for radioactive products and by viewing the plates under ultraviolet light for unlabeled compounds. Preparative tlc for isolation of certain photoproducts utilized ChromAR sheets (1.0-mm thickness, Mallinckrodt Chemical Works, St. Louis, Mo.), prewashed by developing twice in acetone. The sheets were developed in heptane–chloroform–ethanol (7:2:1), and the photoproducts were viewed under ultraviolet light.

Preparation and Isolation of Photoproducts. Analytical grade methazole (0.01 mol; 2.61 g) was dissolved in 2 l. of pesticide quality methanol in an 18-cm diameter crystallizing dish. The stirred mixture was exposed to a germicidal lamp (2 bulbs, General Electric G15T8) by resting the lamp receptacle across the top of the dish. The distance from the lamp to the surface of the liquid was about 2 cm. Methanol was added at 4-hr intervals to bring the solvent up to its original volume. The exposure was terminated after 24 hr since tlc examination of the photolysis mixture at this time revealed that only small amounts of unreacted methazole remained. At least five photoproducts were produced under these exposure conditions (Figure 1). However, an additional product (F, Figure 1) was formed in significant quantity during workup of the photolysis mixture. A concurrent decrease in the levels of photoproduct E suggested that E was a precursor to F, a belief supported by later investigation.

The solvent was stripped from the photolysis mixture and concentrated to about 150 ml by rotary evaporation. Florisil (75 g, 80/100 mesh) was added, and the photolysis products were adsorbed onto the Florisil by evaporating the solvent until no methanol odor was detected. The mixture was placed in a 6.5-cm i.d. glass column containing 100 g of dry Florisil. An additional 100 g of Florisil was added to prevent solvent disturbance of the photolysis products–Florisil layer, and the column was then eluted with petroleum ether–ether (4:1). Twenty 100-ml fractions were collected; fractions 1 and 2 contained crude photoproduct A (0.10 g), while fractions 5–20 contained photoproduct B and unreacted methazole. The column was then eluted with ether to yield a mixture of the two major photoproducts, C and D (1.57 g). These compounds were of very limited solubility in ether, and a total of 12 l. of solvent was required for their elution. Acetone was then passed through the column to elute products E and F and very small amounts of residual C and D.

Crude photoproduct A (a yellow oil) was held in a sublimator at 50° and atmospheric pressure for 12 hr, and light yellow needles of A were collected from the coldfinger. The compound was tlc pure and melted at 42–43°. Attempts to purify the minor photoproduct B were not successful.

The 1.57-g mixture of C and D obtained directly from the Florisil column was crystallized once from boiling methanol to give 0.82 g of white crystalline material containing roughly equal amounts of C and D. This mixture was dissolved in refluxing acetone, (66 parts w/v) and boiling hexane (200 parts w/v) was then added. After 48 hr at −5°, two crystal types were observed, along with clumps of white, fluffy, short needles, and a white granular solid. These crystals were separated mechanically and washed with hexane to yield photoproduct C (white granules, tlc pure, mp 263–266°) and photoproduct D (white needles, about 80% tlc pure, with the impurity being photoproduct C). Product D was purified by two additional recrystallizations from acetone–hexane to give pure white needles, mp 251–254°.

The acetone eluate from the Florisil column containing products E and F was concentrated, and the two compounds were isolated by preparative tlc. The products were further purified by recrystallization from ether–hexane to yield E (tlc pure, mp 141–143°) and F (tlc pure, mp 126–131°).

Photodecomposition of Surface Deposits of Methazole-^{14}C Exposed to Sunlight. Solutions of the three ^{14}C-labeled methazole preparations (3.0 μg in 50 μl of methanol) were pipetted onto the center of 10 × 10 cm glass plates and the solvent was allowed to spread normally. After solvent evaporation, the plates were exposed to sunlight in an unprotected area. Three replicates were run for each label and exposure time. Samples were removed at various intervals from exposure and the residual radiocarbon was recovered by rinsing the plates with 15 ml of acetone. To estimate the levels of radioactivity remaining on

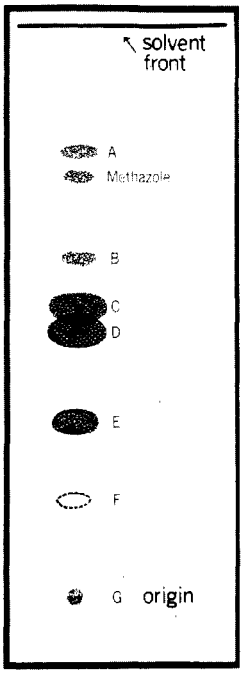


Figure 1. Drawing of a thin-layer chromatogram showing the photodecomposition products of methazole after exposure to ultraviolet light in methanol solution.

the glass surface after the acetone rinse, the plates were washed thoroughly with scintillation cocktail and radioassayed directly. In no case did the scintillation cocktail wash contain greater than 0.5% of the total radiocarbon applied to the glass surface. Aliquots of the acetone rinses were radioassayed by liquid scintillation counting, and then the extracts were concentrated by a gentle stream of nitrogen, spotted on tlc, and the plates were developed as previously described. After exposure of the plates to X-ray film for 5 days, the gel areas corresponding to the darkened spots on the radioautograms were scraped and quantitated by liquid scintillation counting.

Photodecomposition of Methazole-^{14}C in Water. Glass Petri dishes (9-cm diameter) were filled with 60 ml of distilled water, and 6 μg of methazole-phenyl-^{14}C was added in 0.1 ml of methanol. The resulting concentration (0.1 ppm) was well below the 1.5-ppm water solubility limit for methazole. The solutions (three replicates for each exposure interval) were held outside in an unprotected area during daylight hours. Distilled water was added twice daily to compensate for evaporation. For analysis, samples were extracted with chloroform, the extracts were concentrated, and the photoproducts were resolved on tlc as described above.

Toxicity Tests. Compounds C and D were assayed for phytotoxicity to growing pinto bean and cherry tomato plants by topical application of methanol solutions to the dorsal leaf surface. The treated plants were held outdoors and toxicity symptoms (chlorosis of the treated areas) were observed 5 days later. Toxicity of the products to male white mice (Swiss-Webster, 20 g) was evaluated by intraperitoneal injections in 0.1 ml of dimethylsulfoxide. Mortality determinations were made 72 hr after treatment.

RESULTS AND DISCUSSION

Chemical Nature of Photoproducts. Photoproduct A (Figure 1) was identified as 3,4-dichloronitrobenzene on the basis of identical tlc behavior, melting point, ir, ms, and pmr with an authentic sample of the compound. Because photoproduct B was produced only in very small amounts, attempts were not made to determine the chemical nature of this compound.

Photoproducts C and D were two of the three major compounds generated under the exposure conditions employed (Figure 1). The very similar properties of these two compounds on silica gel tlc prevented their quantitative separation, but it appeared that D was the major of the two. The ir spectra of C and D were quite similar, with both showing strong carbonyl absorption in the 1700 cm^{-1} region, and exhibiting strong, broad absorption bands between 2600–3300 cm^{-1}. The mass spectra of C and D (Figure 2) were essentially identical. The "parent" ion at m/e 216 (Cl = 35), which was also the base peak, in each spectrum corresponds to a difference of 44 mass units from the methazole molecule. These data suggested that C and D were isomeric compounds having an empirical formula $C_8H_6Cl_2N_2O$ formed by loss of carbon dioxide from methazole. This was confirmed by elemental analysis. Calcd for $C_8H_6Cl_2N_2O$: C, 44.27; H, 2.79; Cl, 32.67; N, 12.90. Found photoproduct C: C, 44.30; H, 3.01; Cl, 32.65; N, 12.93. Found photoproduct D: C, 44.36; H, 2.89; Cl, 32.81; N, 12.96. The peak in the ms of C and D at m/e 187 corresponds to the loss of NCH_3 or HCO from the parent ions.

Irradiation of each of the three methazole-^{14}C preparations indicated that the phototransformations of methazole to C and D involved the loss of the number 5 carbon of the heterocyclic ring. Both methazole-phenyl-^{14}C and methazole-3-carbonyl-^{14}C decomposed to radioactive compounds corresponding on tlc to C and D; however, exposure of methazole-5-carbonyl-^{14}C under identical conditions did not yield any radioactive photoproducts.

Integration of the pmr spectra of C and D demonstrated only two aromatic protons in each of these compounds, as contrasted to three in methazole. The aromatic signals in C appeared as a "quartet" at δ 6.85–7.25, possibly indicative of adjacent protons on a tetrasubstituted phenyl ring. Those of D appeared as two singlets at δ 7.12 and 7.35, indicating isolated protons. Three proton singlets in the δ 3.5 region of the pmr spectra of C and D indicated that the *N*-methyl group remained intact in each of the products. The pmr of C and D integrate only five protons rather than six, as was predicted on the basis of ms and elemental analysis. Apparently, both C and D contained a hydrogen that did not give a detectable pmr signal under the parameters employed.

Based on the above data, it was concluded that methazole photoproducts C and D were produced by opening of

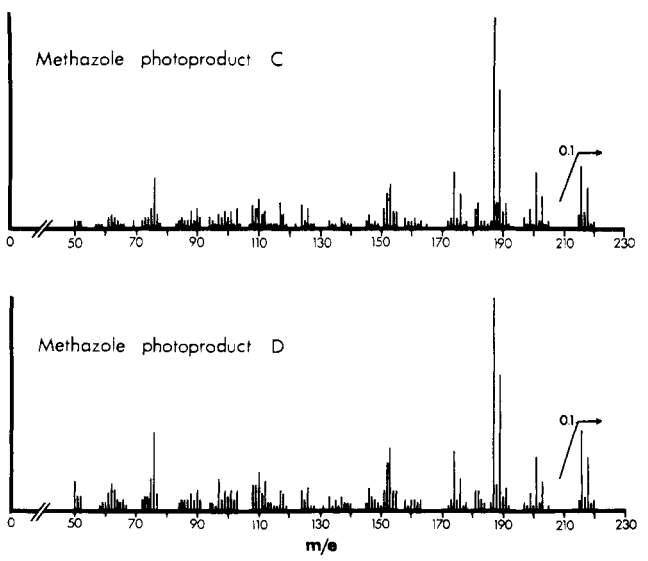


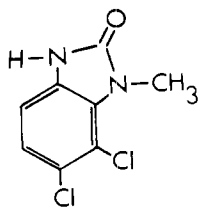
Figure 2. Mass spectra of methazole photoproducts C and D. Peaks under arrow are one-tenth of their actual length.

Table I. Photodecomposition of Methazole-^{14}C on Glass Surfaces Exposed to Sunlight

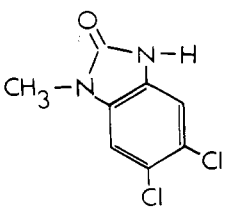
	% of recovered radiocarbon/hr[a]													
	Methazole-phenyl-^{14}C							Methazole-3-carbonyl-^{14}C						
Product	0	.5	1	2	4	8	8 hr dark	0	.5	1	2	4	8	8 hr dark
Methazole	98.4	93.0	93.2	79.8	45.3	41.0	97.3	98.5	93.5	80.8	75.3	36.6	36.4	99.2
A	0	0	0	0	0	0	0	0	0	0	0	0	0	0
B	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C	0.3	1.4	1.3	4.2	9.3	10.8	0.5	0.2	1.3	5.8	6.1	11.5	11.2	0.2
D	0.2	2.1	2.2	6.7	16.0	17.6	0.3	0.1	2.1	8.3	9.5	17.5	18.6	0.2
E_1	0.7	2.3	2.2	6.1	18.2	16.2	1.2	0.9	2.1	2.9	5.7	22.4	18.7	0.3
F	0.1	0.5	0.4	1.6	5.6	7.2	0.4	0	0.3	1.2	1.6	5.5	7.9	0
G	0.1	0.3	0.4	1.6	5.6	7.2	0.2	0	0.3	1.0	1.8	6.5	7.2	0
H	0.2	0.4	0.3	0	0	0	0.1	0.3	0.4	0	0	0	0	0.1

[a] No radioactive photoproducts were detected after exposure of methazole-5-carbonyl-^{14}C.

the oxadiazolidine ring with loss of the number 5 carbon as carbon dioxide, and then recyclization of an intermediate at the 2 or 6 position of the dichlorophenyl ring to form two isomeric 2-benzimidazolinones. Final proof of structure was obtained upon synthesis of 6,7-dichloro-1-methyl-2-benzimidazolinone (C) and 5,6-dichloro-1-methyl-2-benzimidazolinone (D) by reaction of the appropriate dichloro-1-methyl-*o*-phenylenediamine with urea, as described for other analogs (Davoll and Laney, 1960). These syntheses were kindly conducted at our request in the laboratories of Velsicol Chemical Corp. The 2-benzimidazolinones obtained by chemical synthesis were identical in all spectral comparisons to photoproducts C and D.



C



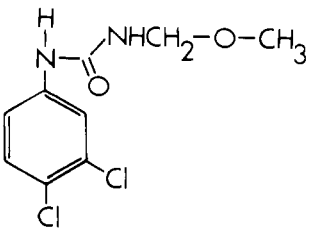
D

Although it seemed possible that C and D might be formed with the methylurea derivative (II) as an intermediate, this was shown not to be the case. Irradiation of a methanol solution of authentic methylurea for extended periods did not result in the formation of either C or D.

Photoproduct E obtained on irradiation of methazole in methanol (Figure 1) was initially suspected to be the methylurea derivative (II) because the two compounds exhibited identical tlc behavior. However, spectral comparisons established that the products were indeed different. The ms of II and E were quite similar, but II showed a very small ion at m/e 218 (Cl = 35), which was absent in the ms of E. Product E gave an apparent "parent" ion at m/e 187 (Cl = 35). This 2-chlorine ion, which was the base peak in the ms of both II and E, was concluded not to be the molecular ion of E, and probably represents a $C_6H_3Cl_2NCO$ fragment. In the case of II, this fragment resulted from the loss of NH_2CH_3.

The ir spectra of II and E were also similar. Both compounds gave two strong NH absorption bands, 3333 and 3368 cm^{-1} in the spectrum of II and at 3273 and 3303 cm^{-1} in the spectrum of E. Also, both compounds exhibited strong carbonyl absorption bands, 1646 cm^{-1} for II and 1673 cm^{-1} for E. The ir spectrum of E showed a strong absorption band at 1055 cm^{-1}, which was absent in the spectrum of II, and possibly was indicative of an ether linkage. The pmr (acetone-d_6) of both II and E integrated three aromatic protons, and the two compounds gave essentially identical aromatic signals. Also, both compounds gave two broad one-proton N*H* signals, centered at δ 5.84 and 8.20 in the spectrum of II, and at δ 6.74 and 8.37 in the spectrum of E. Finally, the *N*-methyl group of II gave a three-proton doublet centered at δ 2.74; whereas, the upfield region of the pmr spectrum of E integrated five protons, a methyl singlet at δ 3.23 and a two-proton doublet at δ 4.63.

It was concluded from the above data that photoproduct E generated on irradiation of methazole in methanol was the following methoxymethylurea derivative.



E

Table II. Photodecomposition of Methazole-phenyl-^{14}C in Water Solutions (0.1 ppm) Exposed to Sunlight

Days of exposure	% of recovered radiocarbon as indicated product										
	Chloroform-soluble										Water-soluble
	Methazole	A	B	C	D	E_1	F	G	H	I	
0	99.2	0	0	0.2	0.1	0.4	0	0.1	0	0	0
1	90.4	0	0	2.8	2.2	2.6	0	0.2	0	0	1.8
2	84.6	0	0	4.5	2.1	3.0	0.2	0.2	0	0.1	5.3
4	75.0	0	0	6.5	2.9	6.7	0.5	0.3	0	0.4	7.7
7	34.2	0	0	9.5	2.7	35.9	0.6	0.2	0	0.5	16.4
7 (dark)	79.3	0	0	0.9	0.6	14.7	0.8	0.2	0	0	3.5

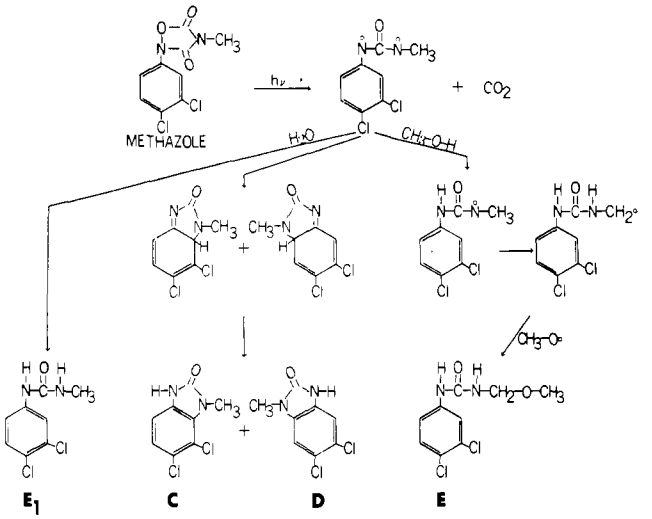


Figure 3. Proposed mechanism for the photodecomposition of methazole.

Lending additional support to the assignment of E as a methanol reaction product was the recent finding by Tanaka *et al.* (1972) that plants metabolized monuron [3-(4-chlorophenyl)-1-methylurea] to an unstable hydroxymethyl intermediate, which was transformed into 3-(4-chlorophenyl)-1-methoxymethylurea when extracted or stored in methanol. Whether the generation of photoproduct E in the current studies involved a short-lived hydroxymethyl intermediate was not established. However, irradiation of authentic methylurea (II) in methanol did not result in the production of photoproduct E. Therefore II would not appear to be an intermediate in the generation of E under the exposure conditions employed.

Final confirmation of the structure of photoproduct E was obtained upon the synthesis of 1-(3,4-dichlorophenyl)-3-methoxymethylurea by the reaction of the corresponding urea with formaldehyde in the presence of methanol (Zigeuner *et al.*, 1951). This synthesis was performed by chemists at the Velsicol Chemical Corp. The methoxymethylurea obtained by chemical synthesis was identical in all spectral characteristics with photoproduct E.

The decomposition of E during workup of the photolysis mixture produced a product (Figure 1, F) that was identical in tlc behavior to the authentic urea (III). Although isolated only in very small quantities, F was identified as the urea on the basis of tlc behavior, ir, ms, and melting point. The fact that photoproduct E partially decomposed during workup was not surprising, since the authentic 1-(3,4-dichlorophenyl)-3-methoxymethylurea decomposed to the urea (III) when allowed to stand on silica gel tlc for several hours.

No attempts were made to isolate or characterize the minor compound(s) remaining at the origin after tlc resolution of the photolysis mixture (photoproduct G, Figure 1).

Photodecomposition of Methazole on Glass Surface. Exposure of methazole-^{14}C to sunlight on glass surfaces resulted in an accumulation of the same major products isolated following photolysis in methanol, except that the methylurea (photoproduct E_1) was a major product and the methoxymethylurea (E) was absent (Table I). Identification of photoproduct E_1 as the methylurea was made on the basis of its cochromatography with the authentic compound in several solvent systems. Although a number of solvent systems failed to separate products E and E_1 on silica gel chromatoplates, the compounds were successfully resolved by tlc on aluminum oxide plates (Merck, F_{254}, Type T, 0.25 mm) developed in 9:1 ethyl acetate–isopropyl alcohol.

Methazole-phenyl-^{14}C and methazole-3-carbonyl-^{14}C were degraded in almost identical fashion. The fact that methazole-5-carbonyl-^{14}C yielded no radioactive photoproducts indicated that the first step in the photolysis of methazole was the loss of the number 5 carbon of the oxadiazolidine ring. Photoproducts A and B, observed as minor components after photolysis in methanol, were not detected on glass. Photoproduct A (3,4-dichloronitrobenzene) probably would not be detected after photolysis on surfaces, even if produced, since it would volatilize quickly. Table I does not reflect volatility losses from the glass, which accounted for as much as 80% of the applied radiocarbon after 8 hr exposure.

The very minor product H, detected in the zero exposure samples (Table I), may not have been a true photoproduct since it was not detected after 1 hr of exposure. Product H migrated on tlc slightly above photoproduct E_1, and no attempts were made to determine its chemical nature. The degradation of methazole-^{14}C observed on glass surfaces exposed to sunlight for short periods was demonstrated to be light dependent, as samples covered with heavy paper and held in the sun for 8 hr showed no significant decomposition (Table I).

Degradation of Methazole-^{14}C in Water. Exposure of water solutions of methazole-phenyl-^{14}C to sunlight resulted in significant photodegradation within 1 day (Table II). The major compound produced was photoproduct E_1 which, at the end of 7 days exposure, comprised approximately 36% of the total chloroform-extracted radiocarbon present. Unlike the previous exposures in methanol or as surface deposits, C and D were produced in relatively low amounts. Also, E_1 was formed in a significant quantity even when water solutions of methazole were held in the dark (Table II). Other than E_1, no methazole degradation products were formed in appreciable quantity when stored in the dark (Table II). The large increase in E_1 observed between the fourth and seventh days of exposure may have resulted from metabolism by microorganisms developing in the water. Photoproduct I, migrating on tlc just below photoproduct D, was detected in minute amounts after 2 days exposure of water solutions of methazole. The chemical nature of photoproduct I or of the radiocarbon remaining in the aqueous phase after chloroform extraction was not investigated.

A mechanism for the photodecomposition of methazole, based on the major products found upon irradiation of methazole in methanol, as deposits on glass surfaces, and in water, is shown in Figure 3. Since products C, D, and E_1 also were generated from a water solution of methazole stored in the dark (Table II), the formation of these compounds is not completely light dependent.

Toxicity of Compounds. Methazole photoproducts C and D were not phytotoxic to bean and tomato foliage when applied to the leaf surfaces at concentrations as high as 30 $\mu g/cm^2$. The minimum toxic dose of methazole, *per se*, was 1.0 $\mu g/cm^2$ for tomatoes and 0.3 $\mu g/cm^2$ for beans. Photoproducts E_1 (methylurea) and F (urea) were not evaluated here, but Jones and Foy (1972) reported that the methylurea was active herbicidally, while the urea was much less effective.

When injected into mice with DMSO as a carrier, the LD_{50} values for methazole, C, and D were 600, 290, and 200 mg/kg, respectively. Products A, C, D, E_1, and F were reported to be of low oral toxicity to rats, the acute oral LD_{50} doses (corn oil carrier) being greater than 500 mg/kg for each product (Whitacre, 1972).

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Parathion: Persistence on Cotton and Identification of Its Photoalteration Products

Ronald L. Joiner*[1] and Karl P. Baetcke[2]

Parathion (*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothioate) was found to be at least 7× more persistent than previously reported on cotton. [^{14}C]Parathion was applied four times in 3 successive weeks to cotton in four environmental situations: environmental growth chamber; greenhouse; controlled-exposure field; and open field. After 28 days, 11.2 to 15.4% of the total radioactivity applied was recovered by methanol extraction and was found to be 58 to 68% unchanged [^{14}C]parathion. There was a constant increase in photoalteration products, coupled with a consistent decrease in [^{14}C]parathion with time. Photoalteration products of parathion present included *S*-ethyl parathion, *S*-phenyl parathion, paraoxon, and *p*-nitrophenol. No previously unreported metabolites were found on cotton foliage. Procedures for the extraction, purification, identification, and quantitation of ^{14}C-radioactivity on cotton are discussed.

Ethyl parathion (*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothioate) has been utilized effectively in the past in insect control. The effectiveness of ethyl parathion is due chiefly to characteristics which are typical of most organophosphorus chemicals: it is highly toxic to target organisms and easily applied as aerosols, emulsifiable concentrates, ultralow volume sprays, and formulated sprays. In addition, ethyl parathion is quick acting, inexpensive, possesses relatively low residual activity, and is a broad spectrum pesticide. An undesirable feature of ethyl parathion is that it is equally toxic to nontarget and target organisms. However, due to the continuing controversy that has developed concerning the widespread usage of persistent organochlorine insecticides, ethyl parathion has come to be regarded as a more desirable chemical for utilization in insect control.

A serious drawback to the replacement of chlorinated compounds with organophosphorus compounds is their high mammalian toxicity. As will be shown later, several incorrect assumptions have been made in the past, including that ethyl parathion can be applied to crops with little subsequent danger to man. Recent evidence, based on a number of poisoning incidents, indicates that some statements concerning the safety of parathion were incorrect.

Kalkat *et al.* (1961) showed that high temperature and high humidity decreased the field half-life of parathion, but increased its toxicity. Lichtenstein and Schultz (1964) reported that one-half of the paraoxon applied to a soil sample had disappeared 5.5 hr after soil treatment (as determined by a colorimetric method) and that parathion, under the same conditions, lost one-half of its residue in just over 6 days. Over this 6-day period, the amount of paraoxon steadily increased, indicating direct conversion of parathion to paraoxon. Coffin (1966) reported a 19-fold decrease in parathion residues in 4 days when sprayed on lettuce, and Hoelscher *et al.* (1968) demonstrated a 15-fold decrease in parathion residue on cabbage before the end of 4 days. El-Rafai and Hopkins (1966) found a half-life for parathion on glass and leaves of slightly more than 1 day, but when concentrations of parathion decreased, paraoxon and *S*-ethyl parathion (isoparathion) increased. Two other degradation products were unidentified.

Light has been implicated as a factor responsible for the breakdown of parathion. Cook and Pugh (1957) reported that exposure of parathion to light results in the formation of cholinesterase inhibitors chromatographically different from parathion. Frawley *et al.* (1958) treated parathion with ultraviolet light and found the resulting compounds to be a mixture of parathion, paraoxon, and other oxidation and degradation products. Studies by Gar and Kipiani (1956) and by Koivistoinen (1963) showed that ultraviolet light clearly accelerated the disappearance of parathion from plants.

Despite the information cited above, which suggests that parathion is short-lived, a number of unexplainable poisonings have occurred in recent years. Quinby and Lemmon (1958) summarized 11 episodes of poisoning from contact with parathion residues involving a total of more than 70 workers who were employed in harvesting, thinning, cultivating, and irrigating such crops as apples, grapes, citrus, and hops. Six of the outbreaks occurred within 2 days of parathion application; however, in five episodes, the poisonings occurred from 8 to 33 days after application. More recently, Milby *et al.* (1964) reported parathion poisonings from 16 separate orchards in California in which there was a mean of 23 days between the last application and the poisonings. These studies, as well as similar reports by West (1964), Holmes (1964), and Durham (1964), when viewed in conjunction with reports already presented on the longevity of parathion residues, indicate that some product other than parathion could be responsible for the poisonings or that the reported longevity of parathion is in error.

Department of Biochemistry, Mississippi Agricultural and Forestry Experiment Station, Mississippi State University, Mississippi State, Mississippi 39762.
[1] Present address: Department of Entomology, Texas A&M University, College Station, Texas 77843.
[2] Present address: National Center for Toxicological Research, Jefferson, Arkansas 72079.