either as an intact molecule (Guenzi and Beard, 1968) or in the form of one of its metabolites, other than DDE, which could be rapidly formed from DDT in the soil. Hsu and Bartha (1976) reported that bound residues of 3,4-dichloroaniline were composed of both hydrolyzable and nonhydrolyzable forms. Therefore, the nature and mechanism of the formation of soil-bound residues of different pesticides may be different.

In the future, it will be important to obtain information about the mechanism of binding of pesticides, thus possibly shedding some light on the mechanism of their potential release and the conditions at which this release might occur. Since not much information is available pertaining to the nature and the potential biological activity of the compounds that are bound, extensive research in this field is highly desirable. In view of the above findings, the expression "disappearance" and "persistence" of pesticides, so widely used during the last two decades, should be reassessed to consider the bound products.

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Laboratory Studies on the Degradation of (the Pesticide) Aldicarb in Soils

Forrest A. Richey, Jr.,* William J. Bartley, and Kenneth P. Sheets

Degradation of aldicarb samples separately ^{14}C labeled at three positions (*S*-methyl, *N*-methyl, and tertiary carbon) in Norfolk sandy loam, Lufkin fine sandy loam, and Lakeland fine sand soils has been studied under laboratory conditions. Extensive fragmentation of the aldicarb molecule was accompanied by recovery of up to 82.8% of the applied radiolabel as $^{14}CO_2$, the amount depending primarily on label position, incubation time, and soil type/pretreatment. Aldicarb sulfoxide and sulfone were the major solvent extracted metabolites. Part of the solvent unextracted radiolabel was isolated in conjunction with the humic and fulvic acid fractions of soil organic matter.

Aldicarb pesticide is used for protection of cotton, potatoes, peanuts, sugarbeets, and sweet potatoes from attack by mites, nematodes, and many other pests. Since aldicarb is soil applied its fate in soils is of particular importance. The degradation of radiolabeled aldicarb in a variety of soil types has been studied under both field (Andrawes et al., 1971; Bull, 1968; Bull et al., 1970; Coppedge et al., in press) and laboratory (Coppedge et al., in press, 1967) conditions. The field studies were performed under environmental conditions similar to those encountered in commercial application of aldicarb pesticide. However, experimental difficulties led to the loss of substantial portions of the applied radiolabel, thereby making it impossible to provide a good accounting of the pesticide's fate in soil. In laboratory studies, Coppedge et al. (1967) have shown that aldicarb is degraded by soil in a manner qualitatively similar to that under field conditions. Evidence has also been obtained (Coppedge et al., in press) that the volatile degradation product is CO_2, but this was not proven nor could much light be shed on the nature of the unextracted soil residues.

Our objective in the studies reported herein was to gain a fuller understanding of aldicarb degradation in soils. Specifically, we sought to identify conclusively the volatile portion of the degradation products and to increase our knowledge of the chemical nature of the fragments not readily extracted from soil. The use of aldicarb samples separately radiolabeled at the *S*-methyl, *N*-methyl, and tertiary carbon atoms was intended to allow inference of the degree of molecular fragmentation accompanying degradation. Figure 1 gives the radiolabel positions for aldicarb (**1**) and its major metabolites aldicarb sulfoxide (**2**) and aldicarb sulfone (**3**).

Research and Development Department, Chemicals and Plastics, Union Carbide Corporation Technical Center, South Charleston, West Virginia 25303.

Table I. Characteristics of Soils Used in Aldicarb Degradation Tests

Soil type	pH	% organic matter	Mechanical anal.		
			Sand, %	Silt, %	Clay, %
Lufkin fine sandy loam	7.1	1.74	59.7	22.0	17.9
Lakeland fine sand	4.6	1.32	97.5	1.2	0
Norfolk sandy loam	4.8	1.56	82.6	8.5	7.4

Table II. Procedural Details for Aldicarb Soil Degradation Experiments

Expt no.	Aldicarb applied as	Soil thickness above/below Aldicarb	Watering regime[a]	Age of soil[c] sample	Radiolabels tested
1	10% on corncob grits	3.6 cm/9.1 cm	2.5 cm/week for 7 weeks	NSL, air dry 2 years	*S*-Methyl
				LFSL, moist 15 days, then air dried	*S*-Methyl
2	10% on corncob grits	3.6 cm/9.1 cm	2.5 cm/week for 10 weeks	LFSL, moist 40 days, then air dried	All 3 labels[b]
3	In solution (water-acetone, 19:1) (~1 ml)	2.5 cm/7.6 cm	Saturated once at 54 days	NSL, moist 10 days, then used moist	All 3 labels
				NSL, moist 10 days, then air dried	*N*-Methyl
4	In solution (water-acetone, 19:1) (~1 ml)	2.5 cm/10.2 cm	None	LFS, moist 6 days, then used moist	All 3 labels

[a] After initial saturation. [b] *S*-Methyl, *N*-methyl, and tertiary carbon atoms. [c] NSL = Norfolk sandy loam, LFSL = Lufkin fine sandy loam, and LFS = Lakeland fine sand.

MATERIALS AND METHODS

Purification of radiolabeled materials and separation and identification of extractable metabolites and radioassays were performed using previously described procedures (Andrawes et al., 1971).

For quantitation of unextracted radioactivity, samples of the soil residue remaining after extraction were subjected to oxidation by potassium dichromate in a mixture of sulfuric and phosphoric acids at 210 °C (Allison, 1960). The resulting $^{14}CO_2$ was swept by a nitrogen stream through a bubbler containing 5% aqueous hydrochloric acid and into a 100-ml gas-washing bottle fitted with a porous fritted diffuser and charged with 50 ml of ethylene glycol monoethyl ether–ethanolamine (2:1, v/v) instead of the series of traps described in the original paper. Soil freshly dosed with ^{14}C-labeled carbaryl gave 94% recovery of radiolabel by this method.

Soil physical characteristics were determined by Dr. Rabindar Singh of West Virginia University and are given in Table I.

Soils were prepared for experiments by screening while still moist to remove particles larger than 2 mm. Each soil tested was placed in a 6.4-cm i.d. glass column having on its bottom a perforated plastic cap lined with 150-mesh stainless steel screen. A layer of soil was then placed in the column, saturated with distilled water, and dosed on its top surface with approximately 5 × 10^6 dpm of ^{14}C-labeled aldicarb diluted with nonradioactive aldicarb. The degree of isotope dilution was adjusted to give a total aldicarb concentration equivalent to 5.6 kg in 1 ha of soil 15.2 cm thick. Additional soil was then added to cover the aldicarb and this soil was saturated with a calculated amount of distilled water. Procedural details for each of the experiments are given in Table II.

Volatiles. For collection of volatiles, the soil column was sealed inside a 13 cm × 28 cm bell jar provided with inlet and outlet ports. This chamber was connected as one of the following series of traps, tubes, etc. (Figure 2) and air was drawn through them at the approximate rate of 7 l./h: Drierite (W. A. Hammond Drierite Co.) tube (removes water from air) → Ascarite (A. H. Thomas Co.) tube (removes CO_2 from air) → metabolism chamber → trap at −15 °C (retains water) → 100-ml gas-washing bottle equipped with fritted glass dispersion tube and charged with 50 ml of ethylene glycol monoethyl ether–ethanolamine (2:1, v/v) (CO_2 trap) → trap at −5 °C → flowmeter → vacuum manifold. The entire contents of each of the traps and of the gas-washing bottle were taken periodically as samples, and aliquots were assayed for radioactivity. The −15 °C trap had been included to condense water vapor and materials of similar volatility. In operation, this

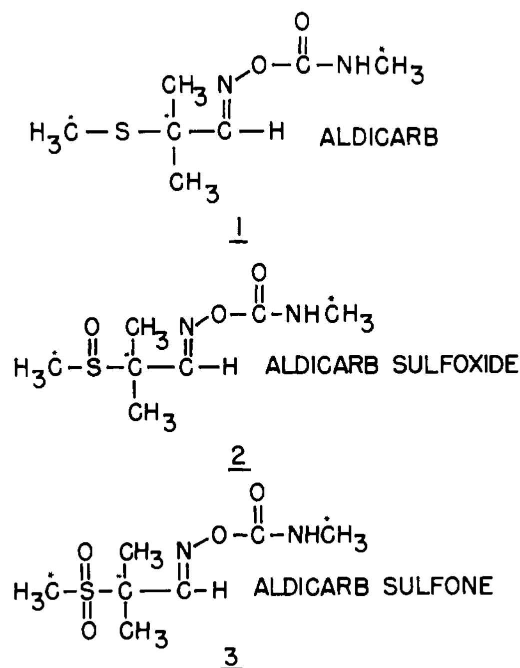

Figure 1. Aldicarb and major metabolites with labeling positions (asterisks).

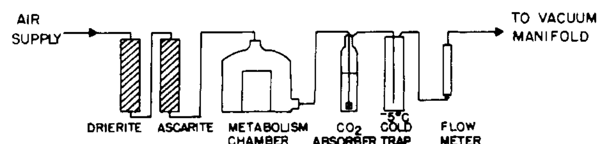

Figure 2. Experimental apparatus used for aldicarb degradation studies.

Table III. Precipitation of $^{14}CO_2$ as $Ba^{14}CO_3$

Time, min	Radioact. in supernatant, % of dose				
	$S-CH_3$	$N-CH_3$	Tertiary	$^{14}CO_2$	Av
5	96	98	98	93	96
30	98	94	94	100	97
150	86	78	75	81	80
1200	20	19	28	18	21
2700	~2	~3	~3	~7	~4

trap recovered very little radioactivity (typically 0.4% of the applied dose during an experiment). Elsewhere, it has been reported (Supak, 1972) that 0.08–0.2% of the dose of aldicarb applied to moist soil is recovered from the vapors during drying. In our experiments a large portion of the radioactivity recovered in the cold trap was lost if the trap was allowed to warm to room temperature unsealed. We suspect that this was loss of CO_2 partially retained by this trap during its operation. In order to quantitate the radiolabel retained by this trap, ethanolamine was routinely added before warming to room temperature and an aliquot of the resulting solution radioassayed. This retention of the radiolabel by basic ethanolamine is support for the tentative identification of $^{14}CO_2$ as the volatile radioactive material retained by the cold trap.

In one experiment the water retained by this trap was extracted and analyzed for total toxic residues (TTR = the sum of aldicarb, aldicarb sulfoxide, and aldicarb sulfone). Only a trace amount (approximately 1% of the radioactivity in the trap or 0.01% of the dose originally applied to the soil) of total toxic residue was present.

Proof of the identity of $^{14}CO_2$ trapped in gas-washing bottles was obtained by treating aliquots of scrubbing solutions from experiments with each of the three aldicarb radiolabels (*S*-methyl, *N*-methyl, and tertiary) and of authentic $^{14}CO_2$ in scrubber solution as follows. A 2.5-ml aliquot of scrubber solution was mixed first with 5.0 ml of 0.2 M Na_2CO_3 (as carrier) and then with 17.5 ml of saturated $Ba(OH)_2$ (an excess). The mixture was stirred and the rate of precipitation followed by withdrawing aliquots and determination of radioactivity in the supernatant. The results of this test are given in Table III.

Although the precipitation of carbonate ion by barium ion is very rapid in water it was discovered that it is slow in mixtures of ethanolamine and water. To make sure that the volatiles were indeed $^{14}CO_2$, an additional experiment was performed using authentic $^{14}CO_2$ in the same solvent mixture. Table III shows that the rate of precipitation is the same for ^{14}C-labeled volatiles from aldicarb as for authentic $^{14}CO_2$. It is concluded that virtually all of the volatile radioactivity collected in the ethanolamine trap is $^{14}CO_2$.

RESULTS AND DISCUSSION

Table IV summarizes recovery of radiolabels in each of the tests performed. In those experiments (no. 2, 3, and 4) comparing metabolism of aldicarb radiolabeled at each of three positions, the amount of radiolabel recovered as volatiles is clearly greatest from the *N*-methyl ^{14}C label. Previous studies with mammals have shown rapid and extensive conversion of [^{14}C]methylamine (Shievelbein and Werle, 1957; Werner et al., 1961) and *N*-[^{14}C]methylcarbamate (Knaak et al., 1965) to $^{14}CO_2$. A species of bacteria has also been shown capable of the former conversion (Kung, 1969). No distinction was seen between the rate of release of volatile radioactivity from *S*-methyl and tertiary ^{14}C-labeled aldicarb samples.

Extracted Degradation Products. In experiments 1 (Table V, Supplementary Material) and 2 (Table VI, Supplementary Material), 2.5 surface cm of water per week was applied to the top of the soil column. Any water eluting was collected and analyzed for radioactive components. At the end of these experiments and experiments 3 (Table VII, Supplementary Material) and 4 (Table VIII, Supplementary Material) the soil was extracted with various solvent systems. Of the various extractants tested, the most effective was acetone–water–phosphoric acid (10 ml:10 ml:1 drop per 10 g of soil). This system was used exclusively for experiments 3 and 4. Table IV summarizes the extracted radiolabel recoveries, while Tables V–VIII (Supplementary Material) provide more detailed time profiles. In a given soil, the amount of total toxic residue extracted is approximately the same for each of the three radiolabels. Since each of the three components of the total toxic residue (aldicarb, aldicarb sulfoxide, and aldicarb sulfone) retains all three labeling positions this is the expected result.

Unextracted Radiolabel. The level of unextracted soil radioactivity detected (Table IV) ranged from a low of 3.1% of the applied dose of *S*-methyl-^{14}C after 12 days in LFS to a high of 16.4% of tertiary label after 69 days in NSL.

We undertook to extract the soil organic matter fractions known as humic and fulvic acids from this latter sample by the procedure of Kononova (1966) which involves se-

Table IV. Summary of Radiolabel Recoveries (as Percent of Applied Dose) from Experiments 1 through 4

Expt no.	Soil	^{14}C label	^{14}C recoveries							Total time, days
				Extracted						
			CO_2	TTR[a]	Others	H_2O sol.	Total	Unextracted	Total	
1	NSL[b]	S-Me	7.1	73.7	15.8	4.1	93.6	4.3	104.0	63
	LFSL[c]	S-Me	82.8	7.9	2.2	0.5	10.6	15.8	109.2	63
2	LFSL	S-Me	42.8	20.1	3.4	4.8	28.3	8.4	79.6	75
	LFSL	N-Me	60.8	22.6	4.4	4.8	31.8	6.9	99.5	75
	LFSL	Tert.	45.1	15.6	5.3	6.8	27.7	11.8	84.6	75
3	NSL	S-Me	22.2	46.1	5.3	6.7	58.1	5.5	85.8	69
3	NSL	N-Me	35.9	38.7	3.8	3.6	46.1	6.1	88.1	69
3	NSL	N-Me[d]	53.9	18.3	0.9	2.8	22.0	6.8	82.7	69
3	NSL	Tert.	21.4	40.0	5.6	6.7	52.3	16.4[e]	90.1	69
4	LFS[f]	S-Me	6.6	21.8	25.1	39.2	86.1	3.1	95.8	12
4	LFS	S-Me	13.2	16.0	22.6	37.2	75.8	3.6	92.6	19
4	LFS	N-Me	53.8	13.7	2.9	5.1	21.7	11.6	87.1	19
4	LFS	Tert.	10.4	16.2	21.2	38.3	75.7	5.1	91.2	19

[a] TTR = total toxic residue = aldicarb + aldicarb sulfoxide + aldicarb sulfone. [b] NSL = Norfolk sandy loam. [c] LFSL = Lufkin fine sandy loam. [d] Soil was briefly air-dried. [e] 9.4% removed by sequential acid-base extraction leaving 7.8%. [f] LFS = Lakeland fine sand.

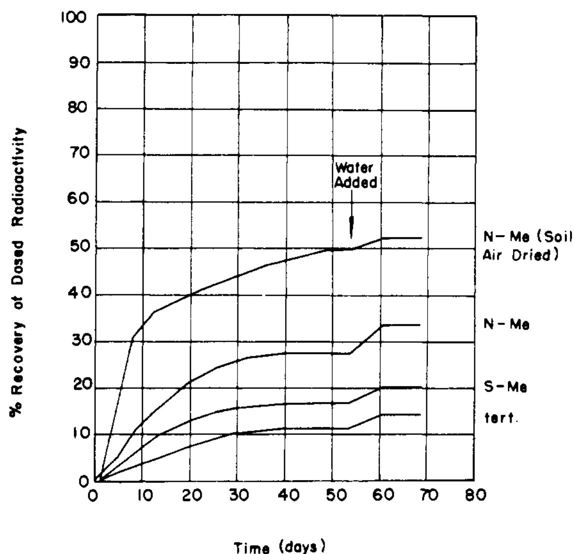

Figure 3. Experiment 3: $^{14}CO_2$ from [^{14}C]aldicarb (three labels) in Norfolk sandy loam illustrating the effects of different soil treatments.

quential extraction with 0.05 N H_2SO_4 and 0.1 N NaOH. Humic acid is precipitated from the basic extract by acidification while fulvic acid remains in solution. In the case under consideration, we recovered 5.5% of the radiolabel associated with the humic acid, 3.9% (of which ~0.25 was organo extractable) in the acidified supernatant and left 7.8% unextracted.

Research by other workers (McLaren and Skujins, 1971) has shown that the ^{14}C label from simple substances (such as glycine and glucose) applied to soil is incorporated into "humic substances" of bacterial origin. Another report (Harvey and Pease, 1973) revealed incorporation of ^{14}C label from methomyl into the humic acid fraction of soil organic matter.

In a preliminary experiment we treated another portion of the above-mentioned soil sample with a mixture of β-glucosidase and cellulase in pH 5 acetate buffer in an attempt to liberate unextracted radiolabel. This treatment resulted in most of the radioactivity being released in organo-extractable form. Thin-layer chromatographic analysis of the released radioactive material showed a number of poorly resolved spots, some of which may correspond to aldicarb metabolites. Positive identification was not possible due to this poor resolution.

Soil Factors. Soil characteristics, soil sample age, pretreatment, and treatment during an experiment were all reflected in the rate of aldicarb degradation or relative proportions of radiolabel recovered in various isolated fractions. A striking difference in rates was seen in comparison of *S*-[^{14}C]methyl aldicarb degradation in Lufkin fine sandy loam (LFSL) stored 15 days (experiment 1) and 40 days (experiment 2). In the former case (Table V, Supplementary Material) nearly 74% of the applied radiolabel was recovered as $^{14}CO_2$ in 22 days. In the latter case only 9.6% was recovered in 21 days.

In experiment 3 a comparison was made of *N*-methyl ^{14}C-labeled aldicarb degradation by soil which had been kept moist since collection and soil which was briefly air dried and then remoistened before dosing. The reason for including a sample of air-dried soil in this experiment was a report (Bartha, 1971) of reduced enzymatic activity in air-dried soil compared to soil which had been stored moist for the same length of time. It was expected that metabolism in the air-dried sample would be less rapid. Instead, as is shown in Figure 3, the metabolism was faster and more extensive based on rate and amount of CO_2 evolution. This may be a result of greater oxygen supply in the air-dried soil which stimulated greater bacterial activity. A similar effect on the rate of CO_2 evolution from soils has been reported (Hesse, 1971). These workers found that if a soil is dried and rewet the rate of conversion of its organic matter to CO_2 is much greater than if the soil had not been dried. This effect was ascribed to release of available organic matter by the drying–rewetting process and a resulting increase of microbial growth. It seems likely that this would stimulate more rapid aldicarb breakdown. After this experiment was 54 days old, CO_2 evolution had declined to nearly zero and the soil was very dry. The soil was rewet at 54 days and a marked increase in collected $^{14}CO_2$ was noted at 61 days (Figure 3). This may also be due to the above-described effect.

In experiment 4 (Tables IV and VIII, the latter contained in the Supplementary Material) all three labels were incubated in LFS and an extra column of soil plus *S*-methyl label was included for early termination in order to compare the distribution of metabolic products during the period of relatively rapid CO_2 evolution with that after this period. The "early termination" experiment showed no marked differences other than higher total toxic residues and lower volatile levels at 12 days from the other *S*-methyl experiment terminated at 19 days.

Relatively more water-soluble radioactivity was recovered from this experiment than from earlier experiments. Whether this is a result of short incubation time or the particular soil used is not known.

CONCLUSIONS

Recovery of CO_2 as the "final" metabolic product from the *S*-methyl, tertiary, and *N*-methyl carbon atoms of aldicarb indicates extensive degradation of the aldicarb molecule to small fragments in soil.

The observed fact that different labels give different degrees of incorporation of radiolabel into the unextracted fraction (Table IV) indicates that a substantial amount of this incorporation occurs after fragmentation of the aldicarb molecule. If any of the radiolabel is incorporated as intact carbamates, the maximum amount of this incorporation in a given soil can be no greater than the least amount of unextracted radiolabel from any of the three labels in that soil. Table IV shows this to be ≤7% of the applied dose of *N*-methyl label after 75 days in LFSL (experiment 2), ≤5.5% of *S*-methyl after 69 days in NSL (experiment 3), and ≤3.6% of *S*-methyl after 19 days in LFS (experiment 4).

Supplementary Material Available: Results of experiments 1–4 contained in Tables V–VIII (4 pages). Ordering information is given on any current masthead page.

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Photolysis of Methyl 2-Benzimidazolecarbamate

James R. Fleeker* and H. Morgan Lacy

Methyl 2-benzimidazolecarbamate (MBC), as a residue on silica gel G, was exposed to sunlight for 30 h. More than 90% of the compound was recovered. MBC in dilute aqueous solution was exposed to sunlight and to light from UV lamps. Less than 10% of the MBC was lost on exposure to sunlight for 40 h, while greater loss occurred if riboflavin or acetone was added to the solution. Photooxidation of the benzene ring of MBC was the predominant reaction detected. Guanidine, carbomethoxyguanidine, and carbomethoxyurea were detected among the photolysis products. MBC was applied to the leaves of corn plants and the plants exposed to sunlight for 18 h. No photolysis products were detected in extracts of the plants.

The benzimidazole fungicides have been shown to be outstanding agents in disease control. An important member of this group of pesticides is benomyl (methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate). This substance decomposes in aqueous solution (Clemons and Sisler, 1969; Krupka, 1974), soil (Baude et al., 1974; Siegel, 1975), plants (Sims et al., 1969; Peterson and Edgington, 1970; Fuchs et al., 1972; Siegel and Zalbia, 1972; Baude et al., 1973), and animal tissue (Gardiner et al., 1968, 1974) to yield another fungitoxic substance, methyl 2-benzimidazolecarbamate (MBC). The decomposition to MBC is also accelerated by sunlight (Kilgore and White, 1970). Clemons and Sisler (1969) considered MBC to be primarily responsible for the fungitoxicity of benomyl preparations. Another fungicide, thiophanate-methyl (1,2-bis(3-methoxycarbonyl-2-thioureido)benzene) also decomposes rapidly in the environment to form MBC (Selling et al., 1970; Vonk and Kaars Sijpesteijn, 1971; Noguchi, 1971; Soeda et al., 1972a,b; Fuchs et al., 1972; Buchenauer et al., 1973; Fleeker et al., 1974).

The metabolism and persistence of MBC have been studied in plants (Siegel, 1973; Ben-Aziz et al., 1974) and soil (Fleeker et al., 1974). In plant and animal tissue, benomyl and MBC show a resistance to cleavage of the methyl carbamate moiety. The benzimidazole ring and methyl carbamate group are slowly destroyed in soil.

Watkins (1974) has reported data on the photolysis of MBC suspended in methanol and exposed to ultraviolet light. After 4 days of exposure, several photodecomposition products were identified in the photolysate. These were: dimethyl oxalate, guanidine, carbomethoxyguanidine, and dicarbomethoxyguanidine. The data reported here concern the photolysis of MBC in dilute aqueous solutions, on corn plants, and as a residue on silica gel TLC plates.

EXPERIMENTAL SECTION

Chemicals. MBC-2-^{14}C-*methyl*-t_3 was prepared from thiourea-^{14}C and methyl-t_3 chloroformate by the procedures of Loux (1961). Methyl-t_3 chloroformate was prepared from methanol-*t* and phosgene (Soeda et al., 1972c). Radiochemical purity by thin-layer chromatography was greater than 99% and specific activity was 7.21 μCi of ^{3}H/mg and 0.61 μCi of ^{14}C/mg. Samples of MBC, 2-aminobenzimidazole, 4-hydroxy-MBC, and 5-hydroxy-MBC were provided by E.I. duPont de Nemours and Co., Inc., Biochemicals Department, Wilmington, Dela. Carbomethoxyguanidine and dicarbomethoxyguanidine were prepared by the methods of Junod (1952). Carbomethoxyurea was prepared using the procedure described by Dains and Wertheim (1920).

Equipment. Samples were assayed for ^{14}C and ^{3}H in a Nuclear-Chicago scintillation counter (Model 6847). Samples expected to show quenching when assayed for radioactivity in this manner were first combusted in a Harvey biological oxidizer. The $^{14}CO_2$ formed on oxidation was collected and assayed in a solution of 500 ml of toluene, 350 ml of methyl Cellosolve, and 150 ml of redistilled ethanolamine containing 5 g/l. PPO (2,5-diphenyloxazole) and 0.5 g/l. dimethyl-POPOP (1,4-bis[2-(5-phenyloxazolyl)]benzene). The ^3H_2O resulting from oxidation was collected and assayed in a solution of one part of Triton X-100 and two parts of toluene containing 5 g/l. PPO and 0.5 g/l. dimethyl-POPOP. A Rayonet Photoreactor, equipped with ten 350-nm lamps, was used in some of the photolysis experiments.

Chromatography. Several solvent systems were used to develop thin-layer chromatograms. For silica gel TLC plates the following solvents were used: *p*-dioxane–formic acid (10:1, v/v), acetone–concentrated NH_3 (97:3, v/v), and ethyl acetate–*p*-dioxane–methanol–concentrated NH_3 (160:20:5:0.5, v/v/v/v). Alumina TLC plates were developed with acetone–concentrated NH_3 (97:3, v/v). Chromatograms of Whatman No. 1 paper were developed (ascending) with 1-butanol–acetic acid–water (120:30:50, v/v/v). At least three of these solvent systems were used in each chromatographic analysis. Radioactivity on chromatograms was detected by cutting the paper or scraping the thin-layer chromatograms in sections and placing the individual sections or scrapings in vials for assay in the scintillation counter. In the chromatography

Department of Biochemistry, North Dakota State University, Fargo, North Dakota 58102.