Photolysis of the Aquatic Herbicide Fluridone in Aqueous Solution

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Photolysis of the aquatic herbicide fluridone has been investigated in several aqueous systems. In laboratory experiments, photochemical half-lives ranged from 22 to 55 h and were only slightly dependent on fluridone concentration, oxygen concentration, and pH. Two benzaldehydes, two benzoic acids, and *N*-methylformamide were identified as major photoproducts. In other experiments using sunlight, the photolysis rates of fluridone were identical in lake and distilled water, and the formation of similar photoproducts in lake water was demonstrated.

Fluridone, 1-methyl-3-phenyl-5-[3-(trifluoromethyl)-phenyl]-4(1*H*)-pyridinone, is an experimental aquatic herbicide under development by Elanco Products Co., a Division of Eli Lilly and Company. Its unique activity against aquatic weeds has been reported previously (Parka et al., 1978; Arnold, 1979; McCowen et al., 1979; Sanders et al., 1979).

Fluridone is applied directly to the water surface or underneath the surface and dissipates rapidly after application. West et al. (1979) observed half-lives of from 1 to 11 days (mean 5 days) for dissipation of fluridone from various ponds, while Muir et al. (1980) found half-lives of from 4 to 7 days during similar experiments. Though some of the observed dissipation was due to adsorption by hydrosoil, both authors suspected that fluridone was degrading in water by another mechanism, possibly photolysis. West et al. (1979) conducted a photolysis experiment using a laboratory light source and observed that the compound was photolabile (half-life, 23 h) in aqueous solution. Muir and Grift (1982) confirmed the photolability of fluridone in pond water and identified and quantified several photodegradation products. In this paper the results of experiments to evaluate further the parameters affecting photolysis of fluridone in water are reported. The results of additional studies to identify and quantify photolysis products are also described.

EXPERIMENTAL SECTION

Chemicals. Technical fluridone (99.5%), [^{14}C]-carbonyl-labeled fluridone (17.89 μCi/mg), ^{14}C uniformly phenyl ring labeled fluridone (2.20 μCi/mg), and *N*-[^{14}C]methyl-labeled fluridone (21.1 μCi/mg) were synthesized in the Lilly Research Laboratories. All three ^{14}C-labeled lots of fluridone were determined to be greater than 99% radiochemically pure by thin-layer chromatography and radioautography.

The photoproduct standards 1-methyl-3-[3-(trifluoromethyl)phenyl]-4(1*H*)-pyridinone (I) (Figure 1) and 1-methyl-3-phenyl-4(1*H*)-pyridinone (II) were synthesized by Lilly Research Laboratories. The photoproduct standards 3-(trifluoromethyl)benzoic acid, benzoic acid, 3-(trifluoromethyl)benzaldehyde, benzaldehyde, and *N*-methylformamide were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were used as received. Potassium ferrioxalate for actinometry was synthesized by using the method of Hatchard and Parker (1956).

Laboratory Photolysis Rate. Water for the photolysis rate experiments was redistilled from glass and saturated with air prior to use. The pH was 6.7, and the dissolved oxygen content was found to be 7.9 ppm by using a dissolved oxygen meter (Yellow Springs Instrument Co., Yellow Springs, OH). Deaerated water, prepared by purging with nitrogen overnight, contained 2.0 ppm of dissolved oxygen.

The buffers at pH 3, 6, and 9 were prepared from solutions of 0.01 M citric acid/sodium hydroxide, sodium acetate/acetic acid, and sodium carbonate/sodium bicarbonate, respectively. Solutions were irradiated in 20-mL glass ampules (Kimble Products, Toledo, OH), which were essentially opaque below 280 nm. Sunlight that reaches the surface of the earth contains no significant radiation below 290 nm (Hirt et al., 1960).

The laboratory irradiation apparatus consisted of a combination of fluorescent sunlamps and black lights and has been described previously (Saunders and Mosier, 1980).

Fluridone solutions were prepared at 1.0 and 0.2 μg/mL in oxygen containing water and at 1.0 μg/mL in nitrogen-purged water and pH 3, 6, and 9 buffers. Twenty milliliters of each solution was pipetted into twelve 20-mL ampules.

The irradiation was conducted by placing ten ampules in the irradiation apparatus. Two ampules were removed for analysis after 4, 8, 16, 24, and 32 h of irradiation. The remaining two ampules were not irradiated and served as positive controls. The light intensity incident on the samples during the experiment was determined by using the ferrioxalate chemical actinometric technique described previously (Saunders and Mosier, 1980).

Identification of Photoproducts. For the initial identification of the major nonvolatile photoproducts, a solution containing 500 μg/mL [^{14}C]carbonyl-labeled fluridone (0.0020 μCi/mL) was prepared in 50/50 (v/v) methanol/water. A 20-mL portion of the solution was irradiated 88 h in the laboratory apparatus.

The amount of radioactivity remaining in the solution after irradiation was determined radiochemically by using techniques described previously (Saunders and Mosier, 1980). The remainder of the photolysis solution was transferred to a 125-mL boiling flask, and the methanol/water was evaporated by rotary vacuum evaporation. The residue was dissolved in a small volume of acetone, and the entire sample was fractionated by TLC. Mobile bands were scraped, eluted from the silica gel with methanol, restreaked on separate plates, and rechromatographed. The purified photoproduct zones were again scraped, eluted with methanol, and subjected to analysis by mass spectrometry.

The results of the initial photolysis experiment suggested the presence of volatile photoproducts, and a second experiment was designed to isolate these products. One gram of fluridone was dissolved in 650 mL of methanol in a Pyrex 1000-mL flask and was then diluted to 1000 mL with distilled water. The flask was stoppered and placed out-

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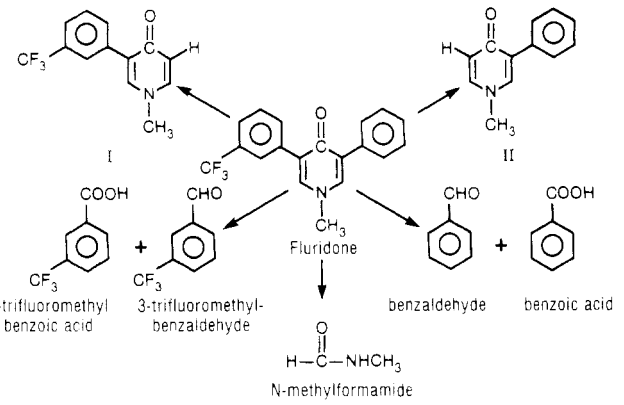

Figure 1. Photolysis products of fluridone.

doors in full sunlight from May 11, 1979, to Aug 3, 1979, near Greenfield, IN. At the end of the irradiation, the solution was analyzed directly by mass spectrometry using a Porapak Q column.

Quantitation of Unidentified Nonvolatile Photoproducts. Fifty-milliliter solutions of each of the three ^{14}C-labeled fluridone standards were prepared at approximately 1.0 ppm in distilled water. Twenty-milliliter portions of each solution were pipetted into each of two 20-mL ampules. One ampule of each pair served as a positive control, and the second was irradiated for 48 h.

All samples were transferred to separatory funnels and were made acidic by the addition of 1.0 mL of 1 N hydrochloric acid. The acidic and neutral photoproducts and the residual fluridone were extracted by partitioning with dichloromethane. The fluridone concentration in a portion of the extract was determined by reverse-phase liquid chromatography. The remainder of the dichloromethane extract was evaporated to approximately 0.5 mL by vacuum rotary evaporation, and the concentrated solution was divided and transferred to two thin-layer chromatographic plates. One plate was developed by using TLC system 1 and the second by using TLC system 2 (see below).

The extracted aqueous solution was transferred to a 250-mL beaker, and the solution was allowed to evaporate at room temperature. The residue was dissolved in methanol and transferred to a TLC plate. This plate was developed by using TLC system 2.

Autoradiograms were prepared and prominent spots were located and scraped into scintillation vials. The photoproducts were eluted directly in the vials by using 5 mL of 80/20 methanol/acetic acid, and the photoproduct content of the solutions was determined radiochemically.

Photolysis in Natural Water. Lake water for the photolysis studies in natural water was obtained from a small eutrophic pond in southern Hancock County, IN. The water was collected near the surface, transported to the laboratory in glass containers, and used immediately. The pH was 8.4.

The exposures of solutions in lake water were conducted in 100-mL glass bottles (Brockway Glass Co., Inc.). The bottles transmitted approximately 20% of the light at 300 nm but were essentially opaque below 280 nm.

For fortification of the water samples, a stock solution of fluridone at 10.0 mg/mL and one of the five photoproducts at the molar equivalent of 1.0 mg/mL fluridone were prepared in ethanol. Individual 100-mL water samples were fortified by injecting 100-μL of the appropriate stock solution into the water sample and shaking to mix the solution.

A total of forty 100-mL water samples were prepared. Twenty contained lake water and twenty contained distilled water. Ten samples of each water type were fortified with fluridone, and the remaining ten with the photoproduct mixture. Two of the ten samples of each water type and chemical composition were positive control samples and were analyzed immediately. The remaining eight samples of each water type and compound treatment were placed outdoors for exposure to sunlight.

All samples were exposed to sunlight between July 2, 1980, and July 28, 1980, near Greenfield, IN. The bottles remained uncapped unless rain was expected. As water was lost from the samples by evaporation, distilled water was added to the samples to return the volume to 100 mL. Two samples of each water type and/or fortification type were taken after 7, 14, 21, and 27 days of exposure and were analyzed immediately.

Analytical Procedures. The contents of ampules from the laboratory photolysis rate study were quantitatively transferred to a separatory funnel. The fluridone was extracted by partitioning with dichloromethane. The extracts were combined in a 125-mL boiling flask and evaporated by vacuum rotary evaporation, and the fluridone was dissolved in the appropriate volume of 70/30 methanol/water for analysis by high-pressure liquid chromatography (HPLC). The instrument employed for determination of fluridone was a Waters Associates, Inc. (Milford, MA), liquid chromatograph equipped with a Model 440 UV detector operating at 254 nm and a 3.9 mm × 30 cm C_{18} μBondapak reverse-phase column. The mobile phase was 70/30 methanol/water, and the flow rate was 0.7 mL/min. Fluridone eluted in approximately 6 min.

Water samples from the fluridone and photoproduct photolysis experiment in natural and distilled water were analyzed by several methods. A 1.0-mL portion of the 100-mL water sample was stored until analysis for NMF directly by single-ion gas chromatography–mass spectrometry. The remaining solution was made basic by the addition of 2.0 mL of 1 N sodium hydroxide, and the fluridone and the aldehyde photoproducts were extracted by partitioning with dichloromethane. The aldehyde photoproduct contents of the extracts were determined by single-ion gas chromatography–mass spectrometry (GC–MS), and the fluridone content of the solution was determined by HPLC as described above. The aqueous solution remaining in the separatory funnel was made acidic by the addition of 4.0 mL of 1 N hydrochloric acid. The two benzoic acid photoproducts were extracted by partitioning with dichloromethane. The benzoic acids were methylated by using diazomethane, and following a 1-hour reaction time at room temperature, the benzoic acid photoproduct content was determined by single-ion GC–MS.

Mass Spectrometry. The initial identification of photoproducts was achieved by mass spectrometry. The instrument employed was an LKB 9000 (LKB, Bromma, Sweden) gas chromatograph–mass spectrometer. The instrument parameters were as follows: ion source temperature, 290 °C; trap current, 60 μA; helium flow, 30 mL/min; electron energy, 70 eV. Samples were introduced via the direct probe or an appropriate GC column.

Photoproducts were quantitated by using the same instrument and a single-ion detection method. For the analysis of benzaldehydes and benzoic acid methyl esters, a 1.8 m × 3.0 mm i.d. glass column packed with 5% Carbowax 20M on 80–100-mesh Chromosorb W-HP and operated at 125 °C was used. The electron energy was set at 20 eV, and the compounds were detected by monitoring the appropriate molecular ion current. For analysis of NMF, the instrument was equipped with a 1.2 m × 3.0 mm

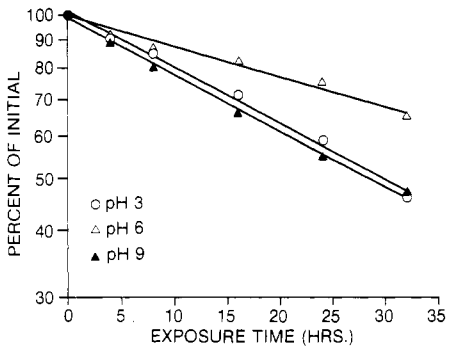

Figure 2. Laboratory photolysis of fluridone in buffer solutions.

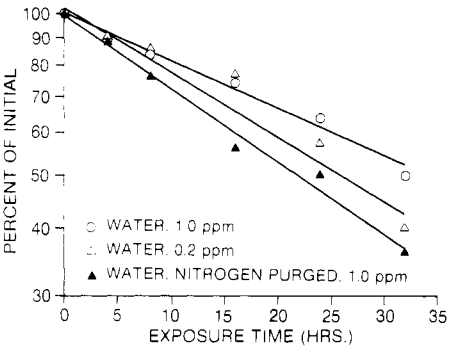

Figure 3. Laboratory photolysis of fluridone in water.

i.d. glass column packed with 80–100-mesh Poropak Q. The oven temperature was 225 °C, the electron energy was 30 eV, and NMF was detected by monitoring the m/e 30 ion current.

Thin-Layer Chromatography. Thin-layer chromatography was conducted on silica gel 0.25-mm plates (E. Merck, Darmstadt, Germany) using 50/50/1 toluene/acetonitrile/acetic acid (TLC system 1) or 75/20/5 dichloromethane/methanol/ammonium hydroxide (TLC system 2) as the developing solvent. Photoproducts were detected by UV adsorption or autoradiography.

RESULTS AND DISCUSSION

Laboratory Photolysis Rate. The results of the fluridone photolysis rate studies are presented in Figures 2 and 3. The data in all aqueous solutions, when plotted on a logarithmic scale, resulted in linear relationships, indicating the photolysis proceeded by first-order kinetics.

Fluridone half-lives calculated from the graphs and photochemical quantum yields are presented in Table I. Half-lives of 30, 55, and 28 h were obtained in pH 3, 6, and 9 buffers, respectively, suggesting a slightly slower photolysis rate in neutral solution than at pH 3 or pH 9.

The half-lives of 34 and 26 h observed in the 1.0- and 0.2-ppm studies, respectively, suggest some depression in the photolysis rate at the higher concentration. This is likely to be due to absorption of the incident light by the fluridone or the photoproducts.

A fluridone photolysis rate study was conducted in nitrogen-purged water to determine if oxygen concentration in the water affected the photolysis rate. Half-lives of 22 and 35 h observed in the nitrogen-purged and aerated waters, respectively, suggested that oxygen may cause a slight decrease in the photolysis rate.

Actinometric measurements conducted during the rate studies verified that no significant variation in the light source intensity occurred during the experiments. The average light intensity was found to be 500 $\mu W/cm^2$.

Identification of Photoproducts. The initial fluridone photolysis study of identification of photoproducts was conducted by irradiating a 500 $\mu g/mL$ solution of [^{14}C]-carbonyl-labeled fluridone for 88 h. Initial TLC data indicated the sample had significantly photodegraded and it was further fractionated by TLC.

Four zones plus some point of application (POA) material were observed. Two of the zones having R_f values of 0.20 and 0.15 were identified as compounds I and II (Figure 1), respectively. Two additional faint zones, with R_f values of 0.4 and 0.5, were also isolated, but sufficient material was not available for a positive identification. The formation of I during photolysis of fluridone in pond water has also been reported by Muir and Grift (1982).

Radiochemical analysis of the sample after photolysis indicated only 47% of the initial radioactivity remained in solution after irradiation. The loss of more than half the radioactivity suggested the presence of volatile photoproducts, and an experiment was conducted to identify them. A methanol/water solution containing 1.0 g of fluridone was exposed to sunlight for 53 days, and the solution was analyzed directly by mass spectrometry using a Poropak Q column. Benzaldehyde, 3-(trifluoromethyl)benzaldehyde, benzoic acid, 3-(trifluoromethyl)-benzoic acid, and *N*-methylformamide were identified and confirmed by comparison of the mass spectra and retention time to those of the authentic compounds.

Quantitation of Nonvolatile Photoproducts. The presence of NMF, benzaldehyde, and benzoic acid photoproducts suggested that fluridone photolysis proceeded by a mechanism which resulted in the complete degradation of the pyridinone ring. Utilization of any one ^{14}C-labeled fluridone sample for a photolysis study could result in formation of photoproducts not containing the ^{14}C label. Such photoproducts would not be detected by using radiochemical techniques. For determination of the presence of all major nonvolatile photoproducts, photolysis experiments were conducted with all three ^{14}C-labeled fluridone samples. Aqueous solutions containing each of the ^{14}C-labeled fluridones were irradiated, the solutions were extracted and analyzed radiochemically, and the extracts were subjected to TLC. Radiochemical results following fractionation by liquid–liquid partitioning and the results

Table I. Half-Lives and Quantum Yields of Fluoridone during Photolysis in Aqueous Solution

solution type	fluridone half-life, h	quantum yield
water, 1.0-ppm concentration	34	0.000043
water, 0.2-ppm concentration	26	0.000057
water, nitrogen purged	22	0.000067
pH 3, buffer	30	0.000049
pH 6, buffer	55	0.000027
pH 9, buffer	28	0.000053

Table II. Distribution of Radioactivity following Fractionation of Photolysis Solutions

sample type	% of initial radioactivity: carbonyl label	phenyl label	*N*-methyl label
aqueous solution	59.3	82.8	98.4
dichloromethane extract	49.4 (29)[a]	72.7 (31)	47.7 (34)
aqueous after extraction	8.6	10.5	52.3
methanol after water evaporation	6.2	7.8	15.4

[a] Numbers in parentheses indicate results of fluridone analysis by HPLC.

Table III. TLC of Fluridone Photolysis Fractions

TLC system	fraction	label position	% of initial fluridone	R_f	identification
1	dichloromethane	carbonyl	29[a]	0.50	fluridone
			1.2	0.00	
			2.8	0.07	I
			6.8	0.30	
		phenyl	31	0.49	fluridone
			14.6	0.31	benzoic acid
		N-methyl	34	0.50	fluoridone
			0.5	0.00	
			1.5	0.06	I
			5.7	0.10	
2	dichloromethane	carbonyl	29	0.80	fluridone
			1.4	0.00	
			2.2	0.08	
			3.6	0.12	
			2.8	0.15	
		phenyl	31	0.81	fluridone
			11.4	0.11	benzoic acid
		N-methyl	34	0.81	fluridone
			0.6	0.00	
			1.8	0.08	
			5.0	0.50	
			1.5	0.64	
	water	carbonyl	2.4	0.00	
			0.3	0.63	
		phenyl	3.0	0.00	
		N-methyl	1.5	0.00	
			1.4	0.04	
			3.0	0.50	
			0.4	0.64	

[a] Percent of initial fluridone is from Table II.

of the HPLC analysis for fluridone are presented in Table II.

In the experiment with the carbonyl-labeled fluridone, only 59.3% of the radioactivity remained following photolysis. Because of the position of the label, the loss of the radioactivity cannot be explained by the volatilization of the benzaldehyde photoproducts. Loss of the label via smaller molecules seems likely, but the nature of these substances could not be determined in these studies.

In the experiment with the phenyl-labeled fluridone, 82.8% of the radioactivity remained following photolysis. This loss of radioactivity here may have been due to the volatilization of benzaldehyde.

In the experiment with the *N*-methyl-labeled fluridone, no significant radioactivity was lost during photolysis, and the majority of the radioactivity was not extractable into dichloromethane but did appear volatile enough to be lost upon evaporation of the water. Similar results were reported by Muir and Grift (1982) during photolysis of *N*-methyl-labeled fluridone in pond water. The nonextractable radioactivity in both experiments is consistent with the presence of the photoproduct *N*-methylformamide. *N*-Methylformamide is not extracted from water with dichloromethane but is lost by volatilization during evaporation of water.

The dichloromethane extracts from the three irradiated aqueous solutions were fractionated by TLC using systems 1 and 2. The methanol solution from the water evaporation was fractionated by using only system 2. The results of the photoproduct quantitation and TLC R_f data are presented in Table III. Only two of the previously identified photoproducts were detected. Compound I was found at 2.8 and 1.5% of the applied amounts in the dichloromethane fraction of the carbonyl- and *N*-methyl-labeled samples, respectively. Benzoic acid was observed

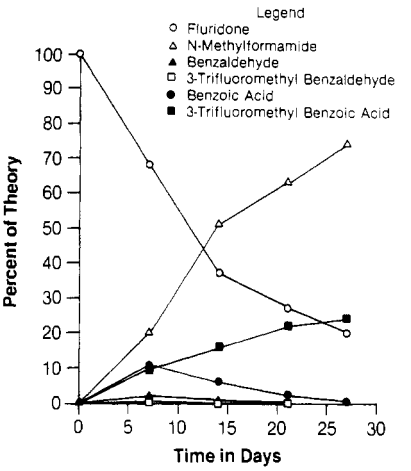

Figure 4. Sunlight photolysis of fluridone in distilled water.

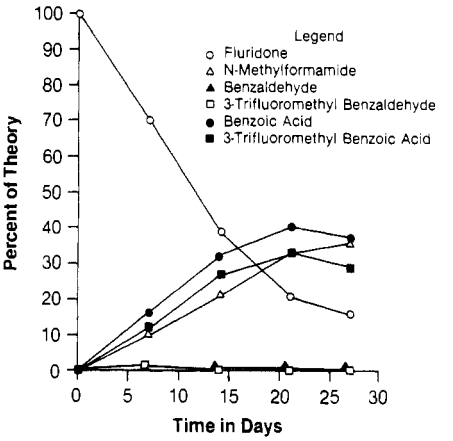

Figure 5. Sunlight photolysis of fluridone in lake water.

at 14.6 and 11.4% of the applied amount in the dichloromethane fraction fractionated by using TLC systems 1 and 2, respectively. (Trifluoromethyl)benzoic acid would not have retained the ^{14}C label and was not detected. The benzaldehyde photoproducts and *N*-methylformamide were too volatile to be retained on the TLC plate.

In addition to the identified photoproducts, a total of 19 unidentified photoproduct zones were observed. Because two TLC systems and three different ^{14}C-label positions were utilized, the zones represent less than 19 unknown photoproducts. Radiochemically, the unidentified zones ranged from 0.3 to 6.8% of the initial amount of fluridone. No unknown photoproduct was present at greater than 6.8% of the initial amount in any of the labeled experiments.

Photolysis of Fluridone in Lake Water. The photolysis of fluridone and formation of the benzaldehyde and benzoic acid photoproducts and *N*-methylformamide were observed in lake and distilled water exposed to sunlight for up to 27 days. In a parallel experiment, the photolysis of each of the five photoproducts was also conducted in lake and distilled water. The results of the fluridone portion of the study are presented in Figures 4 and 5. Fluridone degraded steadily during the experiment with 20 and 16% of the initially applied amount remaining in distilled and lake water, respectively, at the conclusion of the study. There was no difference in the photolysis rates in lake and distilled water.

The concentration of *N*-methylformamide increased steadily throughout the experiment with 74 and 36% of theory, respectively, being present in the distilled and lake water after 27 days of exposure. In distilled water, the

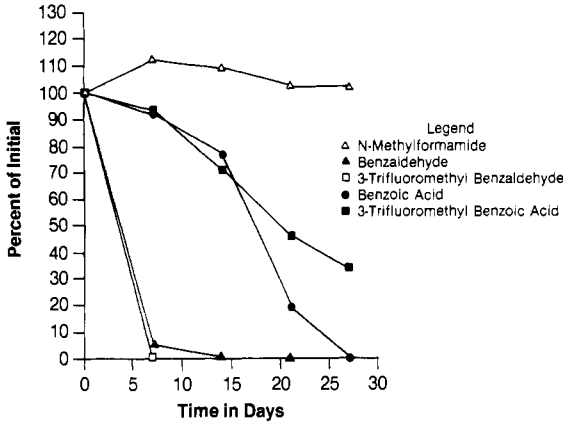

Figure 6. Sunlight photolysis of fluridone photoproducts in distilled water.

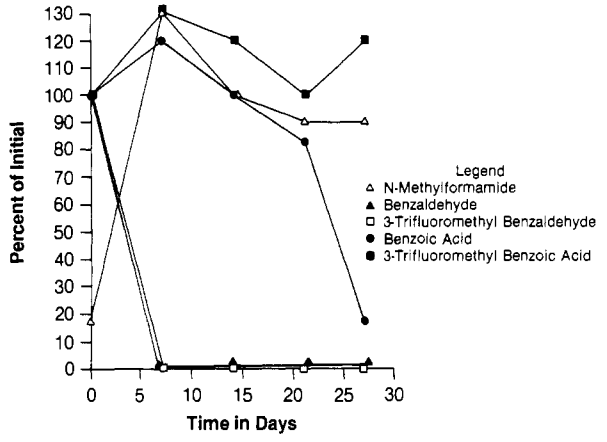

Figure 7. Sunlight photolysis of fluridone photoproducts in lake water.

concentration of 3-(trifluoromethyl)benzoic acid increased steadily to 24% after 27 days, while the concentration of benzoic acid increased initially to 11% after 7 days but then declined to 0.3% after 27 days. In lake water, 3-(trifluoromethyl)benzoic acid and benzoic acid increased steadily, reaching maximums of 33 and 40%, respectively, after 21 days. Only trace amounts of the benzaldehydes were observed in both lake and distilled water after 7 days of exposure, and no benzaldehydes were detected after the 14th day.

The results of the photolysis experiment with the photoproducts are presented in Figures 6 and 7. In both lake and distilled water, the benzaldehydes dissipated rapidly. Only benzaldehyde was detected at 7 days in distilled water, and neither benzaldehyde was observed after 7 days of exposure. The rapid dissipation of the benzaldehydes, whether by volatilization or other mechanisms, accounts for the detection of only traces of these compounds during the photolysis of fluridone.

Both benzoic acids dissipated slowly in distilled water with a maximum of 19% of benzoic acid remaining after 21 days and a maximum of 34% of 3-(trifluoromethyl)-benzoic acid remaining after 27 days. The results in lake water were similar for benzoic acid but suggested that 3-(trifluoromethyl)benzoic acid was more stable as 120% of the initially applied amount remained after 27 days. A number of the determinations of both of the benzoic acids were greater than the initial fortification level, suggesting the possibility that the benzaldehydes may have been oxidized to the corresponding benzoic acids in lake water. The samples were initially fortified with equal amounts of benzaldehydes and benzoic acids.

N-Methylformamide did not dissipate in either lake or distilled water. The results were somewhat variable but clearly showed no significant degradation.

The potential photolysis scheme for fluridone is shown in Figure 1. Little I or II was observed in the laboratory photoproduct quantitation studies, and neither compound was determined in the present lake water photolysis study. The absence of significant amounts of I and II suggested they were formed by a minor photodegradation pathway or that they photodegraded much faster than fluridone so that little accumulated in solution. Mosier (1978) determined the photolysis rates of I and II and found they were approximately as photolabile as fluridone. These results indicate photolysis via formation of I and II is of minor importance.

Shim and Hammond (1976) studied the photolysis of *N*-methyl-4-pyridinone in aqueous solution and concluded that photolysis proceeded by hydration α to the nitrogen and then ring opening. Though no specific mechanism can be postulated, the results of the present studies suggest fluridone photolysis also proceeds by ring opening. The presence of *N*-methylformamide and the benzaldehydes and benzoic acids as major photoproducts as well as significant volatilization losses of ^{14}C during photolysis of carbonyl-labeled fluridone indicates pyridinone ring destruction has occurred.

Registry No. I, 59757-31-2; II, 59757-28-7; fluridone, 59756-60-4; *N*-methylformamide, 123-39-7; 3-(trifluoromethyl)benzoic acid, 454-92-2; benzoic acid, 65-85-0; 3-(trifluoromethyl)benzaldehyde, 454-89-7; benzaldehyde, 100-52-7.

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