Photolysis of Imazapyr (AC 243997) Herbicide in Aqueous Media

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Arsenal herbicide, the active ingredient of which is imazapyr [2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid], is an imidazolinone type of herbicide. Photodegradation of imazapyr ^{14}C labeled at the carboxyl and 5-oxocarbon positions was carried out separately under borosilicate-filtered xenon arc light at 25 °C in aqueous media. Imazapyr was shown to photodegrade rapidly and extensively in aqueous solution. The decline of imazapyr concentration in the solution followed first-order kinetics. The half-lives were calculated as 1.9–2.3 days in distilled water, 2.7 days in pH 5 buffer, and 2.3 days in pH 9 buffer. The predominant photolysis products derived from carboxyl-^{14}C-labeled imazapyr were 7-hydroxyfuro[3,4-*b*]pyridin-5(7*H*)-one and 2,3-pyridinedicarboxylic acid. Decarboxylation was evident as a minor photodecomposition product of carboxyl-^{14}C-labeled imazapyr. Two cyclized compounds, 2,3-pyridinedicarboximide and furo[3,4*b*]pyridin-5(7*H*)-one, were also detected as minor degradates. The one major photolysis product of the 5-oxo-^{14}C-labeled imazapyr was the volatile $^{14}CO_2$.

INTRODUCTION

Imazapyr [2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid] (Figure 1) is the active ingredient of Arsenal, a broad-spectrum imidazolinone herbicide, which is being developed for use in vegetation and forestry management by the American Cyanamid Co. (Los et al., 1983). Imazapyr has been shown to have excellent activity against annual and perennial grass and broad-leaved weeds, vines, and deciduous trees when applied either pre- or postemergence (Ciarlante et al., 1983; Hasui et al., 1983; Orwick et al., 1983a–c) by inhibiting acetohydroxy acid synthase, the feedback enzyme in the biosynthesis of the branched-chain essential acids (Shaner et al., 1984). Similar to other imidazolinone herbicides, imazapyr photodegrades rapidly and extensively in both buffered and unbuffered aqueous solution. Results on the rate of photodegradation and the chemical nature of the photodegradation products of imazapyr are reported.

MATERIALS AND METHODS

Isotopes and Chemicals. ^{14}C-Carboxyl-labeled (Tsou, 1981), ^{13}C-carboxyl-labeled (Hussain, 1981), and 5-oxo-^{14}C-labeled (Zulalian, 1981) imazapyr were obtained from the Agricultural Research Division, American Cyanamid Co., Princeton, NJ. The locations of isotope labels are shown in Figure 1. The specific activities of the ^{14}C-carboxyl-labeled and 5-oxo^{14}C-labeled compounds were 29.91 and 18.68 μCi/mg, respectively, with a radiochemical purity of >99.9% as determined by two-dimensional thin-layer chromatography and autoradiography. For identification of photoproducts of imazapyr, both ^{14}C- and ^{13}C-labeled imazapyr were used. Experiments were performed by using a mixture of one part ^{13}C-labeled imazapyr and one part nonlabeled imazapyr containing sufficient ^{14}C-radiolabeled imazapyr to allow ready detection and measurement of imazapyr and its photodegradation products by conventional radiotracer techniques. By virtue of the $^{12}C/^{13}C$ ratio, the mixture provided doublet ion peaks in the mass spectra of isolated imazapyr and its photodegradation products. These doublets assist in distinguishing ions due to the photodegradation products from those derived from nonlabeled contaminants, even after an extensive and elaborate sequence of purification (Ku et al., 1979; Pohl et al., 1975).

Samples of the following chemical standards were obtained from the American Cyanamid Co. chemical library file: 2,3-pyridinedicarboxylic acid (photoproduct **2**), 2,3-pyridinedicarboximide (photoproduct **3**), and furo[3,4-*b*]pyridin-5(7*H*)-one (photoproduct 4). The potassium acid phthalate buffer (pH 5.0) and boric acid buffer (pH 9.0) were obtained from American Scientific Products, McGaw Park, IL. All other materials were obtained from commerical sources.

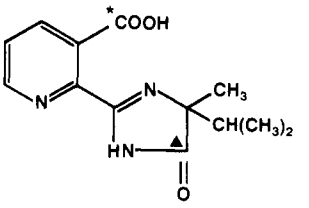

Figure 1. Chemical structure of imazapyr (AC 243997) and positions of isotopic labels. (*) Position of carbon-14 or carbon-13 label at carboxyl position; (▲) position of carbon-14 label at 5-oxo position.

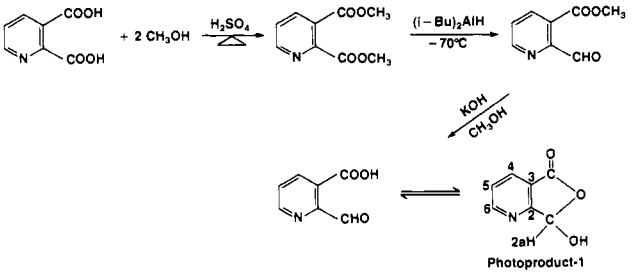

Figure 2. Synthesis of 7-hydroxyfuro[3,4-*b*]pyridin-5(7*H*)-one (photoproduct 1).

Synthesis of 7-Hydroxyfuro[3,4-*b*]pyridin-5(7*H*)-one (Photoproduct 1) (Figure 2). To a 500-mL round-bottom flask equipped with a magnetic stirrer, a heating mantel, and a reflux condenser were added 33.4 g (0.2 mol) of 2,3-pyridinedicarboxylic acid, 130 mL of methanol (large excess), and 15.0 g (0.15 mol) of concentrated sulfuric acid. Sulfuric acid was added cautiously, allowing it to run down the wall of the flask into the swirled reaction mixture. The mixture was heated to reflux overnight and then allowed to cool to room temperature. Excess methanol from the reaction mixture was removed on a rotary evaporator. To the residue was added 75 mL of cold water, and the aqueous phase was extracted twice with dichloromethane. The combined dichloromethane extracts were reduced to 50 mL on a rotary evaporator and washed the same with cold water followed by 5% aqueous sodium carbonate solution. The dichloromethane layer was separated, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give the crude product, a light brown solid. Recrystallization from ether gave 24.4 g

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(62.6%) of white solid crystals of desired product, 2,3-pyridinecarboxylic acid, dimethyl ester, mp 55–56 °C.

Methyl 2-formylpyridine-3-carboxylate was synthesized according to the method of Queguiner and Pastour (1969). To a 1-L three-necked round-bottom flask equipped with an overhead stirrer, a thermometer, and a nitrogen gas inlet were added 19.5 g (0.1 mol) of 2,3-pyridinedicarboxylic acid, dimethyl ester, and 400 mL of dry toluene. The flask was cooled to −70 °C in a dry ice–acetone bath. A mixture of 14.2 g (0.1 mol) of diisobutylaluminum hydride and toluene was added to the flask over a period of 2 h with stirring. Stirring was then continued for an additional 30 min. The progress of the reaction was monitored by the following manner: One milliliter of reaction mixture was rapidly removed and poured into a test tube cooled to −70 °C. Four milliliters of a hydrolysis solution (25 mL of acetic acid plus 6 mL of water plus 50 mL of ether) was added slowly, with stirring. The solution obtained was analyzed for 2,3-pyridinedicarboxylic acid, dimethyl ester, by gas chromatography (GC). Complete disappearance of the ester was necessary because the presence of this compound complicates the purification of methyl 2-formylpyridine-3-carboxylate. According to GC analysis, the reaction was not completed at the end of the stirring period; therefore, another 7.1 g (0.05 mol) of diisobutylaluminum hydride in toluene was added to the reaction mixture. The reaction mixture was stirred for an additional 30 min.

A mixture consisting of 25 mL of acetic acid, 6 mL of water, and 50 mL of ether was then introduced dropwise into the reaction flask over 30 min during which time the temperature was allowed to rise slowly to 10 °C. The solid obtained by filtration was extracted twice with 100 mL of toluene at 80 °C. The filtrate of these two extractions was evaporated under vacuum. Approximately 10 g of oil residue was obtained. The oil was dissolved in 20 mL of 5% sodium carbonate and extracted with toluene. After drying and evaporation of the toluene, extract gave 2.5 g of oil residue. The oil residue was characterized by GC–CIMS. The PICI (CH_4) and NICI (CH_4) mass spectra showed ions at m/z 134$^+$, 166$^+$, and 165$^-$, which corresponded to the (M + H − CH_3OH)$^+$, (M + H)$^+$, and (M$^-$) ions of the desired compound methyl 2-formylpyridine-3-carboxylate. Mass spectral results also showed the presence of other products in the oil. No attempt was made to isolate methyl 2-formylpyridine-3-carboxylate from the mixture, and the crude product was used for the next synthesis step.

Crude methyl 2-formylpyridine-3-carboxylate was subjected to the base hydrolysis. Approximately 100 mg of oil residue was added to 2 mL of 1 N potassium hydroxide in methanol. The mixture was allowed to stand at room temperature overnight. Solvent from the mixture was evaporated, and the residue was redissolved in 1 mL of methanol. The mixture was purified by preparative silica gel thin-layer chromatography. The product was eluted from the silica gel with ethyl acetate. The solvent was evaporated on a rotary evaporator, and white crystals were obtained, mp 192–193 °C. Analysis of the crystals by PPINICI–MS showed ions at m/z 152$^+$, 134$^+$, and 151$^-$, which corresponded to the (M + H)$^+$, (M + H − H_2O)$^+$, and (M$^-$) ions of the desired product. Its infrared spectrum showed a strong C=O absorption at 1750 cm^{-1}. The proton NMR spectrum of the crystals in acetonitrile-d_3 showed the following chemical shifts: 2a(H), 6.57 ppm; 4(H), 8.18 ppm; 5(H), 7.59 ppm; and 6(H), 8.93 ppm. The available spectral information indicated that the product was 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (photoproduct 1).

Irradiation. The experiments were conducted in a Mallory environmental chamber (Mallory Engineering Inc., Salt Lake City, UT) equipped with Atlas xenon arc light systems (Atlas Electric Devices Co., Chicago, IL) using borosilicate inner and outer filters to simulate natural sunlight at 6000 W, at 25 °C. On the basis of manufacturer's specification (Atlas Bulletin No. 1183, 1975), constant light output of 6500 W with the above-mentioned filter combination at 48 cm is 114 340 mW/cm^2 with the following spectral distribution: 1500 (<340 nm); 5750 (340–400 nm); 58 700 (400–750 nm); and 48 400 (>750 nm) mW/cm^2. The output is comparable to noon summer sunlight at Chicago, IL, of 141 800 mW/cm^2 with the following spectral distribution: 1040 (<340 nm); 5260 (340–400 nm); 59 800 (400–500 nm); and 75 700 (>750 nm).

Water solution containing [^{14}C]imazapyr was pipetted into a 125-mL Vycor flask (Corning Glass Works, Corning, NY) containing 50 mL of aqueous solution while stirring on a magnetic stirrer. The solution with a nominal concentration of 25 ppm of imazapyr in the stopper-equipped Vycor flask was stirred continuously while exposed to the xenon arc light for various time intervals. Nonirradiated samples of imazapyr in solution held in darkness in the environmental chamber were experimental controls. The aqueous media used in the study were distilled water, 0.5 M potassium acid phthalate buffer (pH 5.0), and 0.05 M boric acid buffer (pH 9.0).

Recovery of the Radioactivity from the Photolysis Solution. The experimental flask was connected to an ethylene glycol trap, to trap any volatile organic compounds. The ethylene glycol trap was connected to a 3 N sodium hydroxide trap, which was used to trap any carbon dioxide evolved. At time intervals 0 h–10 days, the sodium hydroxide, ethylene glycol, and aqueous media were sampled and assayed for total ^{14}C content.

Extraction of the Radioactivity from the Aqueous Media. At the end of the light-exposure periods, approximately 2-mL aliquots were removed from the experimental flask. The aqueous phase with ^{14}C residues were then reacted with excess amount of 2,2-dimethoxypropane in the presence of catalytic amounts of hydrochloric acid. After the reaction was completed, the end products were methanol, acetone, and ^{14}C-labeled residues. This method allowed the transfer of radioactive components from aqueous phase into organic phase. The methanol and acetone mixture was concentrated on a rotary evaporator. ^{14}C radioactivity in the residue was analyzed by thin-layer chromatography. Control experiments showed no breakdown of imazapyr and its photoproducts during the above procedure. Analyses of samples were conducted under subdued room light to prevent further photolytic degradation.

Isolation and Identification of Photolysis Products. Identification of photolytic products was accomplished by demonstration of identical cochromatography of unlabeled reference compounds with the radioactive spots and, where appropriate, by thin-layer chromatography isolation and purification of the radiocomponents followed by mass spectral and proton nuclear magnetic resonance analysis.

Evolution of carbon dioxide during the experiments was validated by isolating ^{14}C-labeled barium carbonate. The sodium hydroxide trap solution that contained ^{14}C radioactivity was added to water and barium chloride mixture. To this mixture were added a few crystals of potassium carbonate to generate excess carbon dioxide for better precipitation. A white precipitate was separated from the solution. The precipitate was filtered and analyzed for radioactivity by combustion.

Radioanalysis. Samples from sodium hydroxide traps were pipetted into Combusto-Cone sample holders and the samples were combusted in a Tri-Carb Model 306 oxidizer (Packard Instrument Co., Downers Grove, IL). The counting solutions of sample oxidizer were Oxisorb 2 absorber (9 mL) and Oxiprep 2 scintillant (12 mL) (New England Nuclear Co., Boston, MA).

The level of radioactivity in the aqueous phase and the organic fraction was determined by liquid scintillation counting in 10 mL of Aquasol 2 scintillation cocktail (New England Nuclear). ^{14}C radioactivity was measured by liquid scintillation counting techniques using an Intertechnique Multi-Mat system consisting of a Model SL 30 liquid scintillation spectrometer and Microdata 1600 computer (IN/US, Fairfield, NJ).

Thin-Layer Chromatographic Procedure (TLC). Thin-layer chromatography was performed on precoated analytical silica gel 60F254 (0.25-mm thickness) plates and preparative silica gel (1.00-mm thickness) plates (E. Merck Co., Darmstadt, Germany). The following solvent systems were used in the thin-layer chromatographic analysis: (a) n-butanol–water–acetic acid (90/3/3 v/v/v); (b) n-butanone–pyridine–water–acetic acid (70/15/15/20 v/v/v/v); (c) dichloromethane–methanol–water (150/44/6 v/v/v); (d) ethyl acetate–methanol–acetic acid (180/105/15 v/v/v); (e) dichloromethane–n-propanol–water–acetic acid (102/150/24/24 v/v/v/v); (f) dichloromethane–n-propanol–water–formic acid (102/150/24/24 v/v/v/v); (g) dichloromethane–diethyl ether (1/1 v/v). Reference compounds were spotted on plates prior to application of the radioactive solutions. Radiolabeled compounds were visualized by radioautography on

Table I. Major Photodecomposition Products of Carboxyl-^{14}C-Labeled Imazapyr in Distilled Water under Simulated Sunlight

time,[a] days	% of applied radioactivity		
	imazapyr	photoproduct 1	photoproduct 2
0	98.6	0	0
1	82.0	9.5	1.1
2	64.0	19.6	2.8
3	46.6	25.0	8.1
4	33.3	26.9	12.4
5	20.8	31.6	12.2
7	9.0	31.6	20.0
9	4.0	31.8	22.8
10	2.7	29.7	22.7

[a] Twenty-four hour daily exposure to simulated sunlight.

Table II. Percent of Imazapyr Remaining in Distilled Water, pH 5, and pH 9 Buffer Solutions in Photolysis Study with Carboxyl-^{14}C-Labeled Imazapyr

time, days	% imazapyr remaining		
	distilled water	pH 5	pH 9
0	98.6	92.1	91.0
0.75			58.7
1	82.0	61.9	50.6
1.75			30.4
2	64.0	44.2	
3	46.6		18.1
4	33.3	24.8	
5	20.8		
6		16.8	
7	9.0	14.8	
9	4.0		
10	2.7		

Kodak SB-5 single-coated blue-sensitive X-ray film (Eastman Kodak Co., Rochester, NY). The nonradioactive standards were located under ultraviolet light. Quantitation of radioactivity was determined by scraping the radioactive spots from the TLC chromatograms and counting in the Aquasol 2 scintillation cocktail gel.

Mass Spectrometric Analysis (MS). The purified photodegradation products were analyzed by chemical ionization mass spectrometry (CIMS) in both the positive ion (PI) and negative ion (NI) modes on a Finnigan Model 4023 GC–MS–DS equipped with a pulsed positive ion negative ion chemical ionization (PPINICI) accessory (Finnigan Corp., Sunnyvale, CA). The mass spectrometric parameters were as follows: source pressure, 0.4 Torr; source temperature, 250 °C; electron energy, 100–150 eV; conversion dynode voltages, ±3000 V; electron multiplier voltage, 800–900 V; preamplifier range, 10^{-7} amp/V; mass spectrometer manifold temperature, 70 °C. Spectra were alternately acquired at 2 s/scan in the positive ion mode (m/z 60$^+$–600$^+$) and in the negative ion mode (m/z 40$^-$–600$^-$).

Gas chromatography–CIMS (GC–CIMS) analyses were carried out on a 6 ft × 2 mm (i.d.) glass column packed with 3% SP 2100 on 100/120 Supelcoport (Supelco Inc., Bellefonte, PA). Methane was used as the GC carrier gas and as the CI reagent gas. No separator or enrichment device was used. In addition to the preceding mass spectrometer and data acquisition parameters, the following gas chromatographic operating conditions were used: CH_4 flow rate, 15 mL/min; source pressure, 0.4 Torr; injector temperature, 250 °C; GC–MS interface temperature, 200 °C; column oven temperature, 200 °C.

Proton Nuclear Magnetic Resonance (P NMR) and Infrared (IR) Analysis. The purified radioactive photodegradation products and synthesized compounds were analyzed by proton magnetic resonance spectroscopy on a Varian T-60A NMR spectrometer using tetramethylsilane as an internal standard and on a FT-80 NMR spectrometer (Varian Associates, Palo Alto, CA). Synthesized compounds were analyzed for certain functional groups as a neat film or in Nujol on a Model 137 B infrared spectrophotometer (Perkin-Elmer, Norwalk, CT).

Table III. Rate Constant (K) and Half-Life ($t_{1/2}$) Values for ^{14}C-Labeled Imazapyr in Distilled Water, pH 5, and pH 9 Buffer Solutions under Simulated Sunlight

aqueous media	rate constant (K),[a] day^{-1}	half-life ($t_{1/2}$)[a] days	n	r^2
carboxyl carbon-14 label				
distilled water	0.3751(0.1867)[b]	1.85(3.70)[b]	9	0.9904
pH 5 buffer	0.2596(0.1298)	2.67(5.34)	6	0.9782
pH buffer	0.5452(0.2726)	1.27(2.54)	5	0.9898
5-oxo carbon-14 label				
distilled water	0.3069(0.1535)	2.26(4.52)	10	0.9960

[a] Based on 24-h daily simulated sunlight exposure. [b] Based on 12 h of light per day.

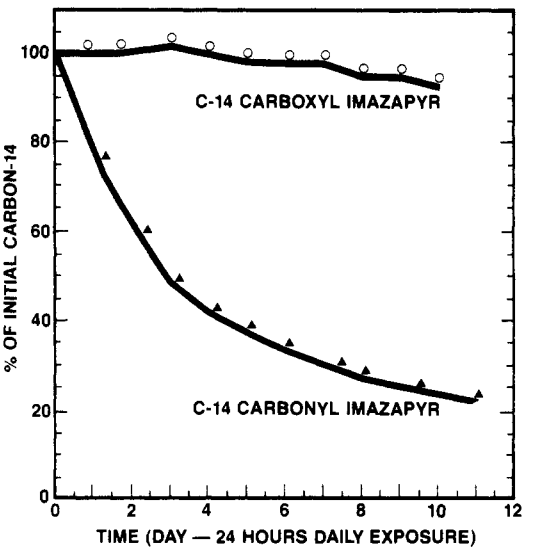


Figure 3. Disappearance of carbon-14 radioactivity from photolysis of imazapyr in water.

RESULTS AND DISCUSSION

Recovery of the Radioactivity from the Photolysis Solution. Data for the recovery of ^{14}C radioactivity in the distilled water after exposure of carboxyl- and 5-oxo-^{14}C-labeled imazapyr in distilled water to simulated light are presented in Figure 3. The data show that 92.5% and 23.4% of the applied radioactivity remained in distilled water by day 10 from carboxyl- and 5-oxo-^{14}C-labeled imazapyr, respectively. Results indicate that most of the radioactivity stayed in the reaction solution in the case of carboxyl ^{14}C label, whereas 76.6% of the applied radioactivity was lost from the reaction solution in the case of 5-oxo ^{14}C label. The volatile ^{14}C radioactivity was trapped by sodium hydroxide. It was shown that the trapped ^{14}C radioactivity was carbon dioxide.

No other ^{14}C volatile organic materials were collected at any time interval during the course of the experiment, indicating volatilization of the parent compound or photodegradation products had not occurred.

Quantitation of Photodegradation Products in Solution. The distribution of major radioactive photodegradation products derived from carboxyl-^{14}C-labeled imazapyr in distilled water with time are given in Table I. After 10 days of continual exposure, only 2.7% of the total ^{14}C radioactivity was found as imazapyr. The results showed that imazapyr steadily photodegraded in distilled water during this time period to two major products, photoproduct 1 and photoproduct 2, accounting for 29.7% and 22.7% of the total ^{14}C, respectively. Two minor radioactive photodegradation components designated photoproduct 3 and photoproduct 4, which were less than 1%

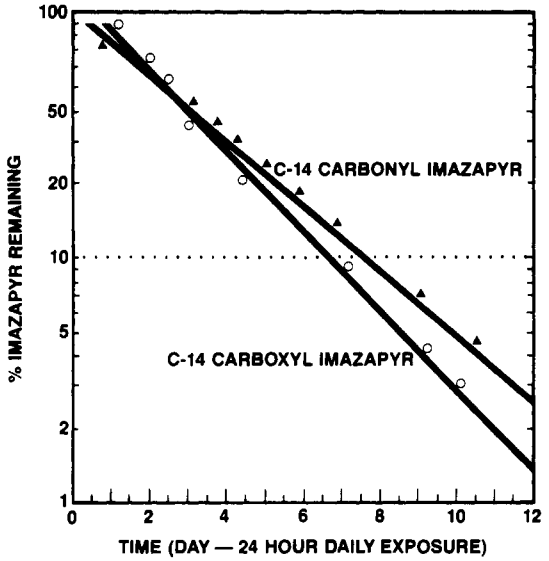


Figure 4. Imazapyr residue decline curve from photolysis study in distilled water.

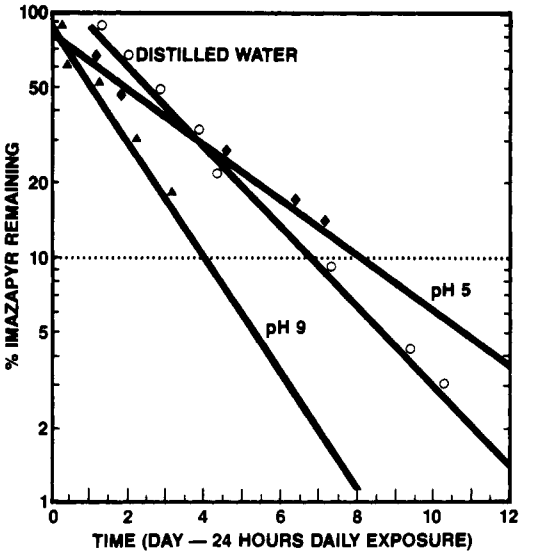


Figure 5. Comparison of photolysis rates of imazapyr in aqueous media.

of the total applied radioactivity at any given time, were also identified. The remaining ^{14}C residues consisted of many minor unknowns with none exceeding 10% of the total ^{14}C radioactivity. Photodecomposition of 5-oxo-^{14}C-labeled imazapyr showed that 4.4% of the total ^{14}C radioactivity was imazapyr at the end of the 10-day interval. Other photoproducts in the water consisted of up to 20 minor unknowns. As with the carboxyl-^{14}C-labeled imazapyr, each unknown accounted for less than 10% of the total carbon-14 residues. One of the unknowns which was further decomposed during isolation appeared as photoproduct of both ^{14}C-labeled imazapyrs.

Parallel control experiments in the dark with carboxyl- and 5-oxo-^{14}C-labeled imazapyr in distilled water, pH 5, and pH 9 buffer solutions showed no breakdown of imazapyr within 10 days of the experimental period.

Photodegradation Rate. The photodegradation rate for imazapyr was determined in distilled water and buffer solutions by using carboxyl- and 5-oxo-^{14}C-labeled imazapyr. The parent compounds recovered at each time interval are shown in Table II. The rate constant (K) was calculated by regression analysis of recovered imazapyr concentration versus time. The half-life ($t_{1/2}$) was calculated by using the equation $t_{1/2} = 0.693/K$. The results of the calculation are given in Table III. It is clear that photolysis of imazapyr in distilled water and buffer solutions followed first-order kinetics (Figures 4 and 5).

Identification of Photoproducts. The radioactivity present in the distilled water was analyzed by thin-layer chromatography. Two-dimensional TLC analysis of the ^{14}C residues derived from both carboxyl- and 5-oxo-^{14}C-labeled imazapyr showed one radioactive component cochromatographed with imazapyr. The product corresponding to imazapyr was isolated by using a preparative silica gel TLC plate and analyzed by GC–MS. The GC–PPINICI (CH_4) analysis showed ion doublet for M^- at m/z 289$^-$, 290– (Figure 6), which confirmed the identity of GC peak as dimethylated derivative of imazapyr [2-(4-isopropyl-1,4-dimethyl-5-oxo-2-imidazolin-2-yl)nicotinic acid, methyl ester]. The dimethylated derivative of imazapyr was generated by dimethylation of imazapyr in the GC injection port by the trimethylanilinium hydroxide (TMAH; TMAH in 0.2 M methanol; Supelco) methylating agent.

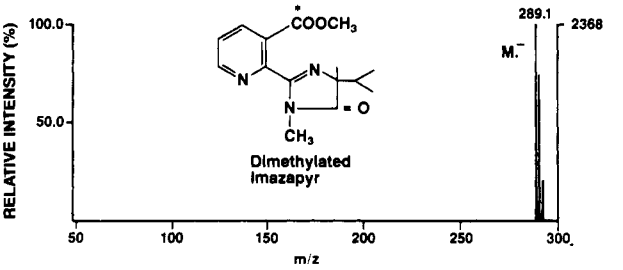
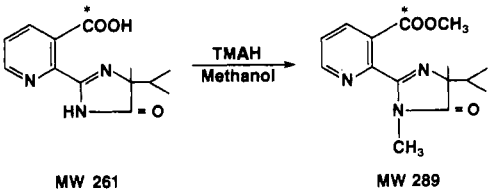


Figure 6. NICI (CH_4) mass spectrum of derivatized imazapyr isolated from the photolysis mixture.



Photoproduct 1 was isolated from the photodegradation radioactive residue on a silica gel TLC plate. The PICI (CH_4) and NICI (CH_4) mass spectra of photoproduct 1 are shown in Figure 7. The isolate showed ion doublets at m/z 152$^+$, 153$^+$, and 151$^-$, 152$^-$, which corresponded to the $(M + H)^+$ and M^- ions, indicating a molecular weight of 151. The assignment of the $(M + H)^+$ ion is supported by adduct ions at $(M + 29)^+$ and $(M + 41)^+$. The m/z 134$^+$, 135$^+$ doublet corresponded to the $(M + H - H_2O)^+$ ion and indicated an OH group which can be readily lost as H_2O from the $(M + H)^+$ ion.

The high-resolution CIMS analysis produced an intense $(M + H)^+$ ion pair at m/z 152$^+$, 153$^+$ with exact masses consistent with the molecular formulas $C_7H_5NO_3$ and $C_6{}^{13}CH_5NO_3$. The high-resolution EIMS analysis showed major fragments at m/z 123$^+$, 124$^+$ ($C_6H_5NO_2^+$) and 105$^+$, 106$^+$ ($C_6H_3NO^+$), which were consistent with the loss of CO and CO + H_2O from the parent ion.

A proton NMR spectrum of photoproduct 1 showed low-amplitude, low-field signals that were of pyridine derivatives. The presence of a free formyl group was not evident. The most likely structure suggested by the spectrum was

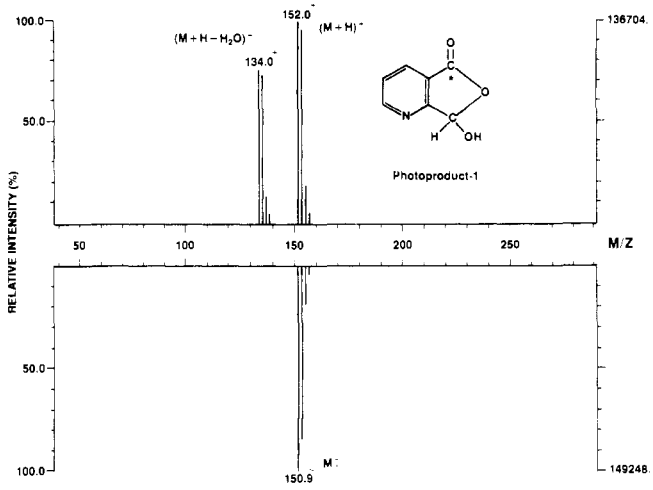
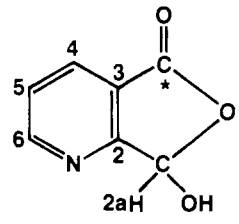


Figure 7. PICI (CH_4) and NICI (CH_4) mass spectra of photoproduct 1.



proton	ratio found	chemical shift (ppm) found
2a (H)	1	6.65
4	1.2	8.22
5	1.1	7.57
6	1.3	8.93

On the basis of the available spectral data information, 7-hydroxyfuro[3,4-*b*]pyridin-5(7*H*)-one was synthesized and found to have identical MS and proton NMR spectra given by isolated radioactive photoproduct **1**. In a two-dimensional TLC analysis, the isolated radioactive photoproduct **1** of carboxyl-^{14}C-labeled imazapyr cochromatographed with synthesized 7-hydroxyfuro[3,4-*b*]pyridin-5(7*H*)-one.

Photoproduct **2** was isolated from the carboxyl-^{14}C-labeled imazapyr photodegradation radioactive residue by using a silica gel TLC plate. The radioactive isolate was methylated with diazomethane in ether. The PICI (CH_4) mass spectrum of this methylated photoproduct **2** is shown in Figure 8. The analysis of the derivative showed ion doublets at m/z 196$^+$, 197$^+$, and 164$^+$, 165$^+$ which corresponded to the (M + H)$^+$ and (M + H - CH_3OH)$^+$ ions and indicated a molecular weight of 195 for the ester analogue. In a two-dimensional TLC analysis, the methylated radioactive photoproduct cochromatographed with 2,3-pyridinedicarboxylic acid, dimethyl ester. The methylated product has to derive from photoproduct **2**. Thus, the photoproduct **2** of carboxyl-^{14}C-labeled imazapyr was identified as 2,3-pyridinecarboxylic acid.

Photoproduct **3** was isolated from the photodegradation residue by using a silica gel TLC plate. Characterization of photoproduct **3** was accomplished without the use of ^{13}C-labeled imazapyr. The PICI (CH_4) and NICI (CH_4) mass spectra of photoproduct **3** are shown in Figure 9. The isolate showed ions at m/z 149$^+$ and 148$^-$. These ions corresponded to the (M + H)$^+$ and M$^-$ ions of a compound with molecular weight of 148 and containing an even number of nitrogen atoms. The isolated photoproduct **3** cochromatographed on TLC with the authentic compound 2,3-pyridinedicarboximide. Photoproduct **4** was tentatively identified by TLC cochromatography as furo[3,4-*b*]pyridin-5(7*H*)-one.

Two-dimensional analysis of the ^{14}C residues derived from 5-oxo-^{14}C-labeled imazapyr on a silica gel TLC plate showed several radioactive photodegradation components. The parent compound imazapyr was identified by cochromatography on TLC. No other radioactive photodegradation products derived from 5-oxo-^{14}C-labeled imazapyr were abundant enough for further characterization.

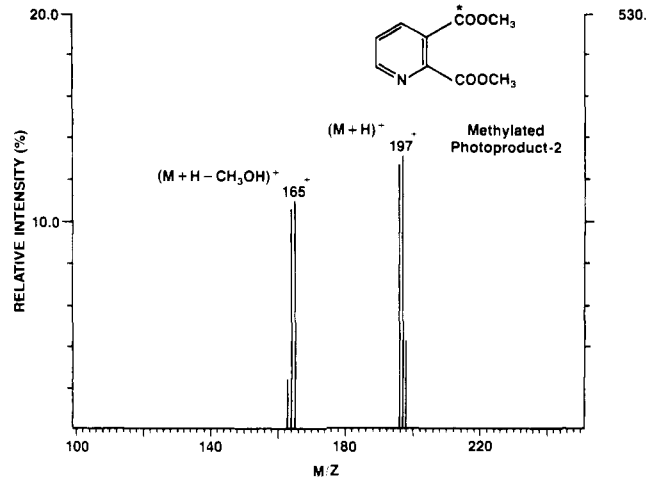


Figure 8. PICI (CH_4) mass spectra of photoproduct **2** after derivatization with diazomethane.

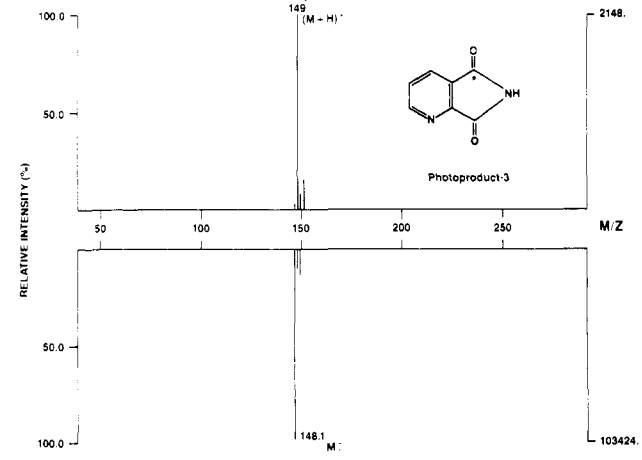


Figure 9. PICI (CH_4) and NICI (CH_4) mass spectra of photoproduct **3**.

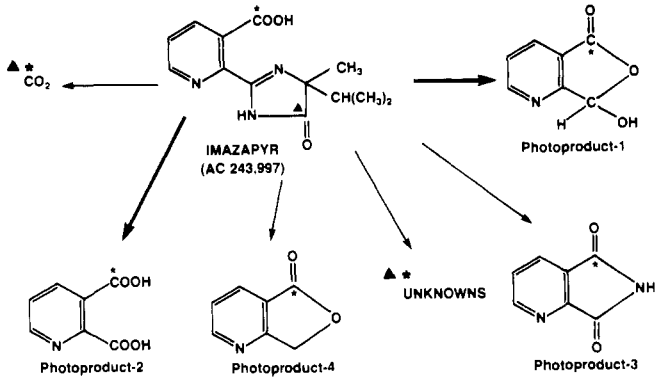


Figure 10. Photolysis of carboxyl-^{14}C-labeled and 5-oxo-^{14}C-labeled imazapyr in distilled water under borosilicate filtered xenon arc light. Separate photolysis studies were conducted for carboxyl-^{14}C-labeled imazapyr and 5-oxo-^{14}C-labeled imazapyr.

In conclusion, imazapyr herbicide photodegraded rapidly in distilled water and in aqueous media at pH 5 and 9 under simulated sunlight. The decline of imazapyr in solution followed first-order kinetics. The photolytic half-life ($t_{1/2}$) of imazapyr in solution is relatively short, ranging from 1.3 to 2.7 days under 24-h continuous light exposure. A slightly higher photolysis rate was observed at a higher pH.

Photodegradation of imazapyr took place at the imidazoline ring. The 5-oxo carbon was rapidly released as carbon dioxide. Two main photodegradates were identified as 7-hydroxyfuro[3,4-*b*]pyridin-5(7*H*)-one and 2,3-pyridinedicarboxylic acid by thin-layer chromatography and mass spectroscopy. In addition, many minor photolysis products, including 2,3-pyridinedicarboximide and furo[3,4-*b*]pyridin-5(7*H*)-one, were also detected. Carbon dioxide was detected as volatile photoproduct which derived mainly from the 5-oxo carbon and to a much lesser degree from decarboxylation of the 3-carboxylic acid (Figure 10).

ACKNOWLEDGMENT

We thank Barbara Knoll for technical assistance in analyzing samples and Patrick Mowery for NMR analyses of samples.

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Received for review July 16, 1990. Accepted September 10, 1990.

Registry No. CO_2, 124-38-9; imazapyr, 81334-34-1; 7-hydroxyfuro[3,4-*b*]pyridin-5(7*H*)-one, 90322-54-6; 2,3-pyridinedicarboxylic acid, 89-00-9; 2,3-pyridinedicarboximide, 4664-00-0; furo[3,4-*b*]-pyridin-5(7*H*)-one, 5657-51-2; 2,3-pyridinedicarboxylic acid dimethyl ester, 605-38-9; methyl 2-formylpyridine-3-carboxylate, 25230-59-5.