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Photodegradation of the Herbicide Imazethapyr in Aqueous Solution: Effects of Wavelength, pH, and Natural Organic Matter (NOM) and Analysis of Photoproducts

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ABSTRACT: The photodegradation of imazethapyr, 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydroimidazol-1*H*-3-yl)nicotinic acid, has been investigated in phosphate buffers and in buffered solutions containing natural organic matter (NOM). Imazethapyr degrades most quickly under 253.7 nm light and at pH values >4. The presence of NOM in solution caused the reaction rate constants for the photodegradation to decrease, with higher concentrations of NOM having a larger effect. Calculations suggest light screening is the major effect of the NOM. Seven photoproducts have been identified, and a photodegradation mechanism is proposed.

KEYWORDS: imazethapyr, imidazolinone, natural organic matter, photolysis, photodegradation, photoproducts

INTRODUCTION

Imazethapyr [5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydroimidazol-1*H*-3-yl)nicotinic acid] (Figure 1) is a herbicide that has been used to prevent weeds in soybeans, peanuts, dry and edible beans, peas, alfalfa, and imidazolinone-tolerant corn since the mid-1980s.[1] The U.S. EPA executed toxicology studies on this compound in 1985, and the first recorded field study was by Talbert et al. in 1987.[2] Imazethapyr can be found in the products Contour, Hammer, Overtop, Passport, Pivot, Pursuit, Pursuit Plus, and Resolve. Imazethapyr is a slightly toxic chemical (LD_{50} = 5 g/kg oral, 2 g/kg dermal, and 3.27 mg/L inhalation, according to the EPA), has a water solubility of 1400 mg/L at 25 °C,[3] and is a weak organic acid (pK_{a1} = 2.1, pK_{a2} = 3.9). The protonation state is important to the sorption on soils and the abiotic degradation of the compound.[4]

Analyzing how imazethapyr reacts physically, chemically, and biologically in the environment requires a vast combination of both photolytic and nonphotolytic studies incorporating crops, soil, groundwater, sediment, river water, and microorganisms. Performance of this compound on crops has been well characterized over the past two decades.[5−8] However, these studies were not concerned with deducing the environmental fate of imazethapyr. Volatilization is not considered to be very significant (<2% from soil), whereas microbial degradation is a significant process that competes with rain runoff.[9,10] Microorganisms have the ability to break down imazethapyr to carbon dioxide molecules, but increased amounts of organic matter (which causes greater adsorption of imazethapyr to soil) and greater rainfall allow a portion of the herbicide to run off into river water.

To date, little research has been conducted in natural environments where imazethapyr is not inherently present. At near-neutral pH, the high solubility of imazethapyr and the anionic structure allow it to have a high mobility in soils and water.[11] In addition, this chemical has been detected at 0.031 mg/L (median) with a maximum of 0.689 mg/L in approximately 71% of Midwestern U.S. surface water samples.[12] Therefore, it is of interest to examine the fate of imazethapyr in water samples. Although the effects on the environmental system at large are unknown, degradation pathways can be studied in a laboratory setting to formulate hypotheses into the fate of such herbicides in aquatic systems.

After the herbicide is washed away from crops by surface runoff, it may react and degrade by various pathways induced by sunlight, radicals, organics, heat, microorganisms, or other environmental factors. Some of these pathways have been examined in the literature.[13−15] Avila et al. examined the fate of imazethapyr in an aquatic environment by studying the photolysis and the reaction of the compound with hydroxyl radicals, one of nature's best oxidizers.[13] However, this paper focused on the fate of imazethapyr applied directly in an aquatic system (rice paddy water) and did not address the fate of the compound in other natural water systems. Elazzouzi et al. have examined photocatalysis of imazethapyr with titanium dioxide and humic acids.[14] However, the authors did not discuss the effects of the wavelength of light and the pH of solution on the photodegradation, focusing instead on the interaction with TiO_2 and humic acids. Ramezani et al. have conducted the most complete analysis of the environmental fate of imazethaypr to date, but did not discuss photoproducts or possible mechanisms of degradation.[15] Despite these investigations, relatively little is known about the photodegradation, occurrence, long-term fate, and water transport of imazethapyr in surface water or groundwater in the United States.

In this work, the photolysis of imazethapyr as a function of wavelength, pH, and the presence of natural organic matter (a model for river waters) has been examined. In addition, the major photoproducts in these systems have been identified, and a mechanism of reaction is proposed. This work provides information and data to better understand the environmental fate of imazethapyr in surface waters.

MATERIALS AND METHODS

Chemicals and Instrumentation. Imazethapyr (purity = 99.5%) was purchased from ChemService and used as received.

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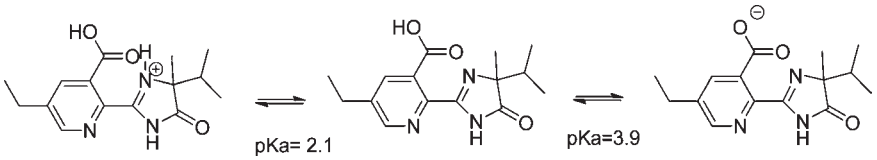

Figure 1. Imazethapyr, an imidazolinone herbicide.

All chromatographic solvents, acetonitrile (ACN), and water, were >99.9% (HPLC grade) and were purchased from Sigma-Aldrich. Phosphate buffers were prepared using H_3PO_4, $NaH_2PO_4 \cdot H_2O$, or $NaHPO_4 \cdot 3H_2O$ (all from Fisher Scientific) as needed in Milli-Q water. All buffers were 1 mM in total phosphate. All natural organic matter (NOM) was obtained from the International Humic Substance Society (IHSS) collected from the Suwannee River (1R101N).

HPLC analysis for imazethapyr was performed with Varian equipment (410 autosampler, 210 delivery system, and 325 UV−vis detector) and a Discovery RP Amide C16 reversed-phase column with 150 mm × 4.6 mm i.d. and 5 μm particle size. All sample injections had volumes of 40 μL. The isocratic mobile phase consisted of 55% aqueous 1.7 mF phosphoric acid buffer (pH ∼2) and 45% ACN with a flow rate of 2.0 mL/min and a run time of 3.0 min. The detector was set at 220 nm.

Hydrolysis in Buffered Solution. Buffered samples of imazethapyr (4.98×10^{-5} M) were placed in 40 mL amber vials at 9, 20, and 30 °C. The temperatures were controlled by keeping the vials in a refrigerator, a room temperature water bath, or a heated water bath. Once per week, an aliquot (1.5 mL) of each sample was removed and analyzed in triplicate via HPLC against a set of imazethapyr standards.

Photolysis Using Artificial Light. Photochemical reactions were conducted using aliquots of imazethapyr (10 mL) in quartz test tubes held in a Rayonet RPR-100 photochemical reactor with a merry-go-round (Southern New England Ultraviolet Co.). Samples were irradiated with eight 35 W low-pressure mercury lamps that emit light centered at 253.7 or 310 nm. The 253.7 nm lamps are nearly monochromatic, whereas the 310 nm lamps have a spectral distribution with a full width at half-maximum of 40 nm. The lamps were uniformly distributed around the vessel, and each sample was irradiated for ≤15 min. Each sample of imazethapyr was prepared by dissolving the desired amount of solid in phosphate buffer, followed by sonication for 15 min. Imazethapyr solutions made in this way were then divided into 13 test tubes. In a given experiment, the initial concentrations of imazethapyr were held constant, typically at a value between 3.5×10^{-5} and 7.0×10^{-5} M. Experiments were also performed using solutions of imazethapyr with 1.0−10 mg/L NOM. In every experiment, potential radical reactions were immediately quenched with 1 mL of isopropyl alcohol upon removal from the RPR-100. Controls without NOM were tested and analyzed in the same fashion as the samples. Nonirradiated imazethapyr samples were employed as dark controls.

Photolysis Using Sunlight. Outdoor photolysis experiments were conducted in St. Peter, MN, on the Gustavus Adolphus College campus (44° 20′ 0″ N, 93° 58′ 0″ W) on July 3, 2008, and July 14, 2008, from 10:20 a.m. to 5:20 pm. The average temperature of a control sample (Milli-Q water) during that time period was 34.5 °C. Samples (15 mL) were placed in quartz test tubes in a 4 × 6 in. black Rubbermaid notecard box at an upward angle of 45° with the open ends facing east. Buffered samples (pH 7) tested were 5.50×10^{-5} M imazethapyr with 9.2 mg/L NOM, 5.12×10^{-5} M imazethapyr with 1.6 mg/L NOM, 6.71×10^{-5} M imazethapyr with 5.0 mg/L NOM, and 4.98×10^{-5} M imazethapyr. At 30 min time intervals, an aliquot (1.5 mL) of each sample was removed and placed in an amber vial for storage and eventual HPLC analysis. The amber vials were immediately stored in the refrigerator (at 9 °C) after removal; analysis of the samples was typically conducted within 2 h of collection and was always completed within 24 h.

Preparation and Analysis of Photoproducts. A 5.11×10^{-5} M solution of imazethapyr in pH 7 phosphate buffer was irradiated under 253.7 nm lamps in the RPR-100 for up to an hour. Samples were collected at well-spaced time points, including several at early time points (initially samples were collected every 30 s with intervals increasing to 5−10 min as irradiation continued). Samples were analyzed on an Agilent 1100 series LC coupled with a Varian 320 MS. The chromatographic separation was performed with tandem 4.6 × 150 mm Zorbax Eclipse XDB-C8 columns. The separation gradient utilized was 10% methanol in pH 6 0.1% formic acid to 50% MeOH over 5 min, then to 90% MeOH from 5 to 7 min, and back to 10% MeOH at 7.01 min. The flow rate was 1.5 mL/min, with an injection volume of 100 μL and a 10 min run time. The LC flow rate into the MS was 200 μL/min. The needle voltage on the ESI was 2 kV, and the nebulizing gas (N_2) pressure was 55.0 psi.

Targeted peaks were separated into individual vials and were analyzed using LC-TOF-MS analysis to obtain empirical formulas. Samples were run on an HP 1100 LC coupled to a Bruker micrOTOF-Q mass spectrometer. The chromatographic separation was performed with a Waters Sunfire C18 chromatography column (2.1 mm × 100 mm, 3.5 μm particle size), with acetonitrile (ACN)/0.1% formic acid and water/0.1% formic acid solvents following a gradient (10% ACN for 3 min, from 10 to 75% ACN over 2 min, 75% for 2 min, from 75 to 90% ACN for 1 min, 90% ACN for 3 min, and back to 10% ACN over 1 min) for a total of a 15 min run. The flow rate was 0.25 mL/min, and the column temperature was 25 °C. The acquisition in the micrOTOF-Q was m/z 50−1000 with positive ionization electrospray.

With several photoproducts nominally identified, HPLC and ESI-MS-MS were used to further analyze the photoproducts and to help elucidate a possible mechanism of photodegradation of imazethapyr. First, a sample of 5.12×10^{-5} M imazethapyr in a pH 6.9 phosphate buffer was irradiated with 253.7 nm light for 10 min. The sample was analyzed with an Agilent 1100 series HPLC using a 100 μL injection at 0.25 mL/min through a C18 column (2.1 × 150 mm, 3.5 μm packing size) using an ACN/0.1% formic acid solvent following a gradient (from 5 to 50% ACN over 9 min, from 50 to 90% ACN from 9 to 12 min, and back to 5% ACN at 12.01 min) for a total of a 15 min run. The detector was a Varian 320 LC-MS instrument with ESI. The ESI parameters were electrospray voltage, 4.5 kV; capillary voltage, 30 V; capillary temperature, 300 °C; and N_2 sheath gas, 55.0 psi. The selected parameters for the MS were a 14 min run time with the

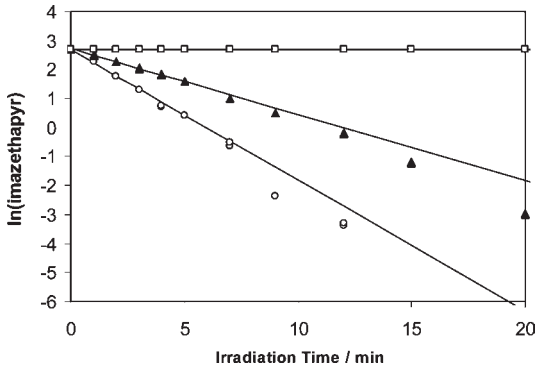

Figure 2. Degradation kinetics of 5.20×10^{-5} M imazethapyr under 253.7 nm lamps (○), 310 nm lamps (▲), and 350 nm lamps (□). The solid lines are weighted linear regression fits to the data. The slopes of these fits are the first-order reaction rate constants: 0.45 ± 0.04 min^{-1} for 253.7 nm lamps, 0.23 ± 0.02 min^{-1} for 310 nm lamps, and 0.001 ± 0.001 min^{-1} for 350 nm lamps.

first quadrupole separating the m/z ratios of 180.0, 194.2, 203.0, 218.0, and 262.0 with a mass peak width of 1.0 amu. The parent peaks were then fragmented using a CID (Ar) gas and collision energy of 10 or 15 V. The third quadrupole was set to scan from m/z 50 to m/z 5 greater than the parent peak. Each mass had a dwell time of 0.1 s.

Rate Constant Data Analysis. All reported pseudo-first-order rate constants were obtained from weighted linear least-squares analysis of the experimental data (regressing ln[C] versus time, where C equals the molar imazethapyr concentration). The weighting factors used for the regression (typically $1/\sigma_Y^2$, where σ_Y^2 is the variance on each value of ln[C]) were set equal to C^2 due to the transformation of variable.[16] The use of this weight reduces the effect of the later time points (which are likely to have greater variance and error) on the fit of the regression line, yielding more accurate reaction rate constants. Rate constants given in the text and tables below are listed as experimental value plus or minus the standard deviation of the slope from the linear regression.

RESULTS AND DISCUSSION

Imazethapyr Hydrolysis. According to the literature, the hydrolysis of imazethapyr is minimal at pH 7.[3,15] Over a period of 90 days, our data verified this result, as no noticeable hydrolysis occurred at 9, 20, or 30 °C. Thus, because imazethapyr is relatively stable in water and is only weakly absorbed to soil,[3,13] photolysis is likely a primary abiotic pathway for degradation in buffered solution, natural water sources, or other environmental matrices. This is consistent with the findings of other authors with other imidazolinone pesticides.[15,17,18]

Wavelength- and pH-Dependent Direct Imazethapyr Photolysis. Each photolysis trial showed imazethapyr degrading exponentially, suggesting a first-order or pseudo-first-order reaction mechanism (Figure 2). Because several authors have reported no significant effects of variations in concentration on the degradations of other imidazolinone compounds, concentration effects were not examined here.[17,19,20] In buffered solutions at pH 7, imazethapyr degraded quickly when irradiated at 253.7 nm (0.45 ± 0.04 min^{-1}), degraded moderately at 310 nm (0.23 ± 0.02 min^{-1}), and degraded very slowly at 350 nm (0.001 ± 0.001 min^{-1}) (Figure 2). The difference in degradation rates with the different lamps is due to differences in photon flux and energy of

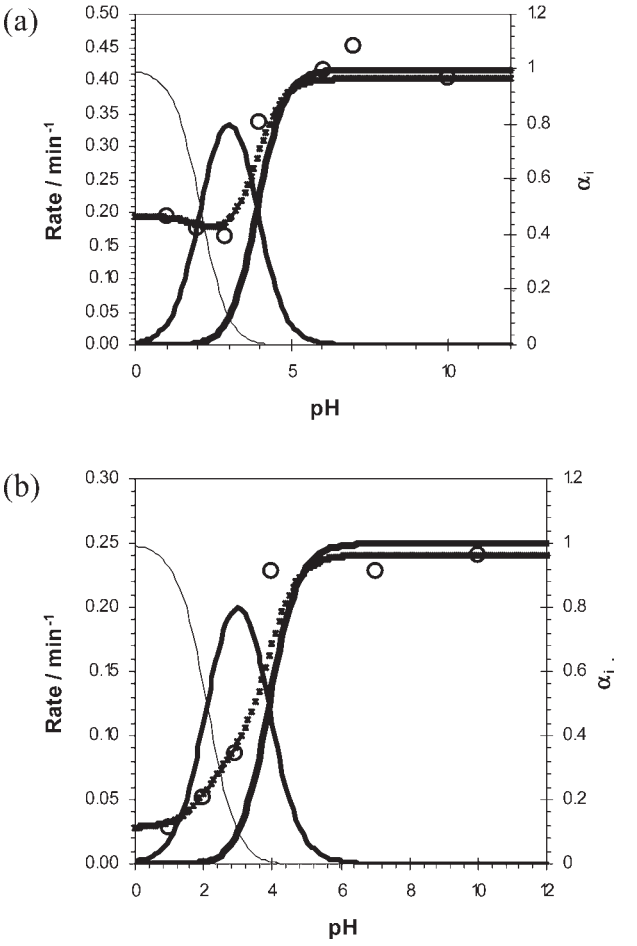

Figure 3. Degradation rate constants and fractional composition of imazethapyr as a function of pH: (a) irradiation with 253.7 nm lamps; (b) irradiation with 310 nm lamps; ○, experimental rate constants; ∗, model ($k_{obs} = \Sigma_i k_i[I]_i$) fit to the experimental rate constants. The solid lines represent the three forms of imazethapyr as shown in Figure 1.

the photons. Due to the slow decay with the 350 nm lamps, all further photolysis experiments in the RPR-100 were conducted with 253.7 or 310 nm lamps.

The pK_a values of imazethapyr are 2.1 and 3.9: the first pK_a is for the protonation of the imidiazolinone ring, and the second is for the ionization of the carboxylic acid.[3] Because this compound can exist in several forms, experiments were conducted in phosphate-buffered 5.12×10^{-5} M imazethapyr solutions with pH values ranging from 2 to 10. An additional experiment was conducted at pH 1 using a 0.1010 M standardized HCl solution as solvent. These experiments were conducted with both the 253.7 and 310 nm lamps in RPR-100. Figure 3 shows the fraction of each imazethapyr species as a function of pH. Overlaid on the plots are the first-order kinetic rate constants for the degradation of imazethapyr under the 253.7 nm lamps (Figure 3a) and under the 310 nm lamps (Figure 3b). As can be seen, the rate constants increase with increasing pH until a pH of approximately 4. At higher pH values, the rate constant plateaus. Thus, the anionic form of imazethapyr undergoes photodegradation with the fastest rate under both sets of lamps. Barkani et al. also found this for imazaquin; the authors showed that the carboxylic group should not intervene directly in the degradation, but the mechanism is favored for the anionic species.[19] Other authors have

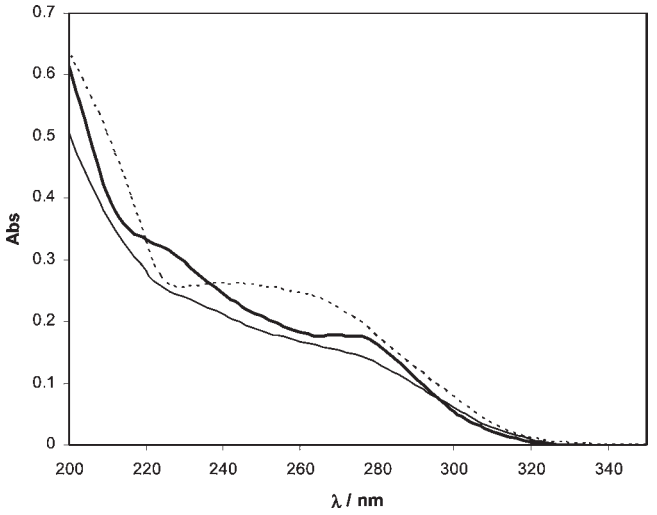

Figure 4. UV−vis spectrum of 5.25×10^{-5} M imazethapyr at pH 2.0 (- - -), pH 3.1 (—), and pH 6.6 (**—**).

observed this trend for imazapic[17] and imazapyr,[18] but our data contradict those of Avila et al. for imazethapyr.[13] There is a difference in trends as a function of pH for the two lamps at low pH; under the 253.7 nm lamps, the neutral form of imazethapyr reacts the most slowly, whereas the cationic form of imazethapyr reacts the most slowly under 310 nm lamps. This has not been reported in the literature, and although it is not completely clear why this difference exists, the difference in molar absorptivity at 254 nm over the pH range may be one explanation (see Figure 4 illustrating the UV−vis spectra of imazethapyr at pH 2.0, 3.1, and 6.6).

The model fit in Figure 3 shows the pH dependence of the overall rate constant as a function of the concentration and rate constant for each imazethapyr species (Figure 1) as given by eq 1

$$k_{obs} = \sum_i k_i [I]_i \qquad (1)$$

where k_i is the photodegradation rate constant and $[I]_i$ is the concentration of each imazethapyr species, *i*. Implicit in this model is the assumption that the photodegradation rate constant of each imazethapyr species is the same at different pH values and that any observed dependence of the photodegradation rate constants on pH will be related to the species distribution as a function of pH. Because the photodegradation rate constant for each species, k_i, depends on two variables, the rate at which light is absorbed by the system and the efficiency of transformation of the species in the system, both of which are pH independent for a given species in a simple matrix,[21] this assumption is justified. The model fits the experimental rate constants well, showing that despite the differences in trends under the two sets of lamps, the observed photodegradation rate constants change with pH due to the changing species concentrations. In addition, natural water systems are typically in the near-neutral range (pH values of 5−9); it is at these pH values that imazethapyr degraded most quickly (for both sets of lamps), suggesting that imazethapyr should be fairly easily removed from natural water systems by photodegradation. (Note, however, that the removal of imazethapyr from natural water systems would be slower than that observed in the laboratory due differences in wavelength and light intensities between the sun and the lamps used in the laboratory.)

Photolysis of Imazethapyr in NOM Solutions. NOM is found in all river waters, commonly at concentrations between 1 and 10 mg/L,[22] but the structure and exact chemical makeup of NOM vary due to soil type, location, biological degradation, and other factors. The NOM used in this study, Suwannee River NOM, contains 52.47% C, 4.19% H, 42.69% O, 1.10% N, and 0.65% S by mass; the oxygen in the NOM consists largely of carboxylic acid character (charge density at pH 8 is 9.85 mequiv/g C).[23] Like other NOM, the Suwannee River NOM should be negatively charged at pH values of 6−9 due to the carboxylic acids.[24]

It has been shown that under some circumstances, the presence of NOM in water samples increases photodegradation rates.[25,26] Typically this is attributed to the ability of NOM to absorb UV light to produce reactive oxygenated species such as hydroxyl radicals or singlet oxygen. However, the light screening due to NOM can also cause photodegradation rates to decrease.[14,15,27−29] Table 1 gives the results of experiments analyzing the effect of NOM on the photodegradation rates of imazethapyr. The addition of 1.6 mg/L to a pH 7 phosphate-buffered 5.25×10^{-5} M imazethapyr solution did not affect the rate constant for the degradation of the imazethapyr. Higher concentrations of NOM (5.0 or 9.2 mg/L) lead to a decrease in rate constants. Thus, it seems that there is very little (to no) photosensitization due to the NOM in these solutions, and the major effect of NOM on the degradation of imazethapyr is light screening. This is contrary to the findings in two literature papers on imazethapyr,[14,30] but supports the findings of Ramezani et al.;[15] the differences are likely due to the variation in source and properties of the NOM used.

Figure 5 gives several UV−vis spectra; Figure 5a gives the UV−vis spectra of three NOM/pH 7 phosphate-buffered solutions (1.6, 5.0, and 9.2 mg/L NOM), and Figure 5b gives the UV−vis spectrum of imazethapyr (5.25×10^{-5} M) and three imazethapyr/NOM solutions (5.25×10^{-5} M imazethapyr with 1.6, 5.0, and 9.2 mg/L NOM), all buffered at pH 7. The Suwanee River NOM absorbs light at wavelengths below 400 nm; at lower wavelengths, the absorbance values increase with decreasing wavelength (Figure 5a). Comparisons of solutions containing imazethapyr with or without NOM (Figure 5b) show that at all wavelengths, the solution containing only imazethapyr had the lowest absorbance and the absorbance of the solutions containing NOM and imazethpyr increased with increasing NOM concentrations. Thus, when both imazethapyr and NOM are in solution, the light reaching the pesticide will be reduced due to the NOM.

The effect on the degradation rate constants due to this light screening can be calculated using the following analysis (see Schwarzenbach, section 15.3[24] for mathematical details and MacManus-Spencer et al.[31] and Grandbois et al. [32] for application to other environmentally relevant sytems). First, a screening factor can be calculated from eq 2

$$S(\lambda) = \frac{1 - 10^{-D(\lambda)\alpha(\lambda)z_{mix}}}{2.3 z_{mix} D(\lambda)\alpha(\lambda)} \qquad (2)$$

where $S(\lambda)$ is the screening factor, $D(\lambda)$ is the distribution function (equal to 1 for the samples in quartz test tubes), z_{mix} is the vertical distance in a mixed body of water (equal to 1 for the

Table 1. Experimental (k_{obs}) and Light Screening Corrected (k_{corr}) Rate Constants for Irradiation of pH 7.0 5.25×10^{-5} M Imazethaypr/NOM Solutions at 253.7 and 310 nm

	253.7 nm			310 nm		
solution	k_{obs} (min^{-1})	$S(\lambda)$	k_{corr}(min^{-1})	k_{obs} (min^{-1})	$S(\lambda)$	k_{corr} (min^{-1})
imazethapyr	0.45 ± 0.04			0.23 ± 0.02		
imazethapyr + 1.6 mg/L NOM	0.47 ± 0.03	0.966	0.49 ± 0.03	0.26 ± 0.02	0.987	0.26 ± 0.02
imazethapyr + 5 mg/L NOM	0.35 ± 0.02	0.922	0.38 ± 0.02	0.22 ± 0.01	0.950	0.23 ± 0.01
imazethapyr + 9.2 mg/L NOM	0.33 ± 0.02	0.813	0.41 ± 0.02	0.21 ± 0.01	0.907	0.23 ± 0.01

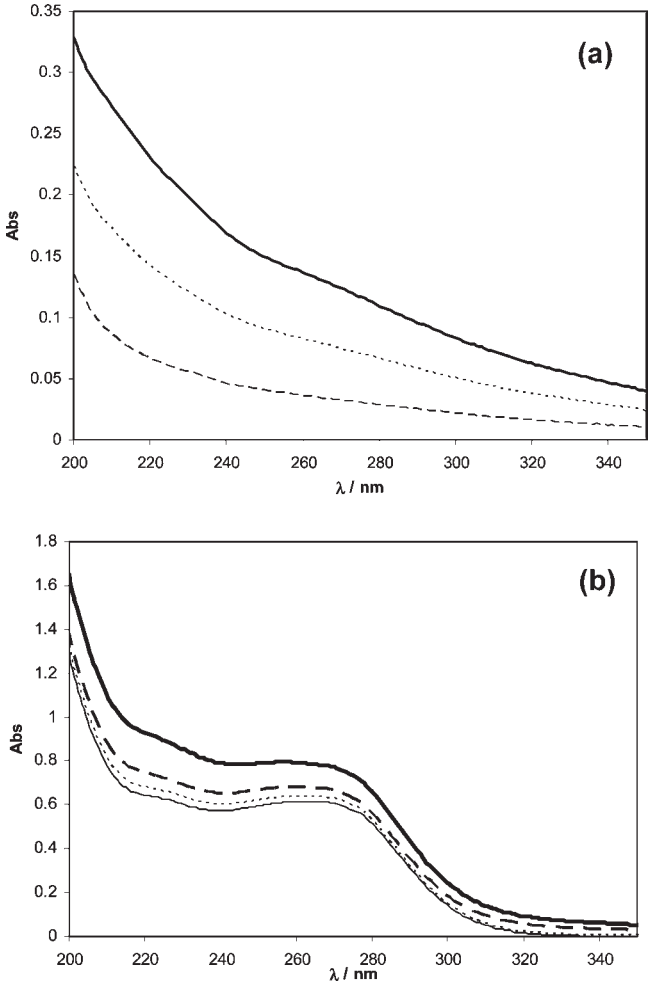

Figure 5. (a) UV−vis spectra of 1.6 mg/L NOM (- - -), 5.0 mg/L NOM (· · ·), and 9.2 mg/L NOM (—); (b) UV−vis spectra of 5.25×10^{-5} M imazethapyr (—), 5.25×10^{-5} M imazethapyr with 1.6 mg/L NOM (· · ·), 5.25×10^{-5} M imazethapyr with 5.0 mg/L NOM (- - -), and 5.25×10^{-5} M imazethapyr with 9.2 mg/L NOM (—).

samples in quartz test tubes), and $\alpha(\lambda)$ is the attenuation coefficient of the medium. $\alpha(\lambda)$ can be obtained from the UV−vis spectrum (Figure 5) and the Beer−Lambert law:

$$A(\lambda) = [\alpha(\lambda) + \varepsilon_i(\lambda)C_i]l \quad (3)$$

$A(\lambda)$ is the absorbance of the solution, $\varepsilon_i(\lambda)$ is the molar absorptivity of imazethapyr, C_i is the concentration of imazethapyr, and l is the path length of the light in the solution. Assuming that the lamps used have a narrow wavelength range, the photodegradation rate constants obtained in the presence of NOM can be corrected for light screening by dividing the constants by the screening factor (eq 4)

$$k_{corr} \approx k_{obs}^{NOM}/S(\lambda) \quad (4)$$

where k_{obs}^{NOM} is the experimental degradation rate constant for imazethapyr in the presence of NOM and k_{corr} is the photodegradation rate constant corrected for light screening. Table 1 provides the experimental photodegradation rate constants of imazethapyr degradation in buffer and three NOM solutions, the screening factors for the given NOM solution and appropriate wavelength, and the photodegradation rate constants of imazethapyr in the three NOM solutions corrected for light screening. As Table 1 illustrates, corrections for light screening cause the photodegradation rate constants in the presence of NOM to match (within experimental error) the photodegradation rate constant of imazethapyr in buffered solution. This shows that the decrease observed in experimental rate constants can be sufficiently explained by light screening. Given the number of assumptions in the calculation (e.g., narrow wavelength range from the lamps and nonturbid, well-mixed samples), these values are in reasonable agreement. These calculations illustrate that light screening has an effect on the photodegradation rate constants of imazethapyr in the NOM solutions and would likely have an effect on degradation of the compound in natural water systems.

Adsorption of imazethapyr to the NOM could be another explanation for the observed reduction in photodegradation rate constants of imazethapyr with increasing NOM concentrations. However, the data do not support this hypothesis. First, the UV−vis spectra presented in Figure 5 show that the absorbances of the NOM/imazethapyr solutions are roughly equal to the sum of the NOM and imazethapyr solutions alone, suggesting that the two species have not changed their photochemical properties upon mixing. Second, there was no drop in free (i.e., nonadsorbed) imazethapyr concentrations (as measured by HPLC) with the addition of NOM to the 5.25×10^{-5} M imazethapyr solutions. Finally, the literature on the sorption of organic molecules to NOM suggests that imazethapyr is unlikely to adsorb to NOM at the conditions used in this paper. At pH 7, the pH used in this study, both the NOM and the imazethapyr are negatively charged,[3,24] and it has been shown that negatively charged organic species will adsorb more weakly than the related neutral compound to anionic NOM.[24] In addition, studies specific to the imidazolinones in soil give soil/water partition coefficients at pH 7 of approximately zero;[33] these authors conclude that all soils studied showed very weak adsorption for imidazolinones at pH values >6. In conclusion, although adsorption is a possible explanation for the decrease in imazethapyr

Table 2. Experimental (k_{obs}) Rate Constants for Irradation of pH 7.0 Solutions in Sunlight

solution	k_{obs} (min^{-1}) / 10^{-3}
4.98×10^{-5} M imazethapyr	6.9 ± 0.5
5.12×10^{-5} M imazethapyr/1.6 mg/L NOM	5.5 ± 0.4
6.71×10^{-5} M imazethapyr/5.0 mg/L NOM	5.5 ± 0.2
5.50×10^{-5} M imazethapyr/9.2 mg/L NOM	4.6 ± 0.2

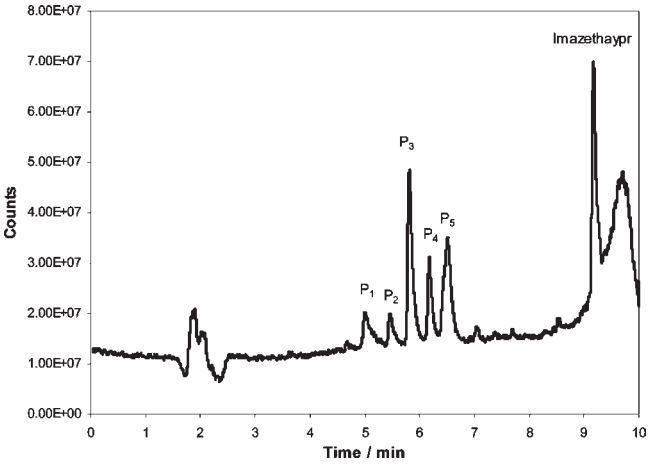

Figure 6. LC-MS chromatogram obtained after 6 min of irradiation of 5.12×10^{-5} M imazethapyr with 253.7 nm light.

photodegradation rate constants with increasing NOM concentrations, it seems unlikely.

Outdoor Imazethapyr Photolysis. Outdoor photolysis produced much lower rate constants due to the lower light intensity and higher wavelengths of UV light (Table 2). The data suggest that at the wavelengths and intensity of light emitted by the sun, degradation of imazethapyr is relatively slow but under appropriate conditions would still be effective (the half-life of imazethapyr in the phosphate-buffered solution was 101 min and in the 9.2 mg/L NOM solution was 152 min). As in the laboratory experiments, the outdoor photolysis of imazethapyr was affected by light screening. However, due to the wide distribution of wavelengths emitted by the sun and wide fluctuations in light intensity, calculations taking light screening into account are difficult to compute.

Photoproduct Analysis. LC-MS was used to follow the degradation of imazethapyr and the formation of photoproducts during the photolysis of a 5.12×10^{-5} M, pH 7.0, buffered imazethapyr solution irradiated under 253.7 nm lamps in the RPR-100. Figure 6 is a representative example of one of the collected chromatograms; the sample shown here was irradiated for 6 min. The peak at retention time 9.2 min is imazethapyr. The other five peaks on the chromatogram are photoproducts: P_1, P_2, P_3, P_4, and P_5 at retention times 5.00, 5.46, 5.83, 6.21, and 6.52 min, respectively. Figure 7 shows the evolution of those photoproducts and the elimination of imazethapyr over time. After 17 min of irradiation, all of the imazethapyr has degraded. At 30 s of irradiation, P_3, P_4, and P_5 have already appeared, and by 24 min, these photoproducts are themselves degraded. P_1 first appears after 4 min of irradiation, and P_2 first appears after 6 min of irradiation; both of these photoproducts are also degraded over time. P_6, not shown on the chromatogram, appears late in the

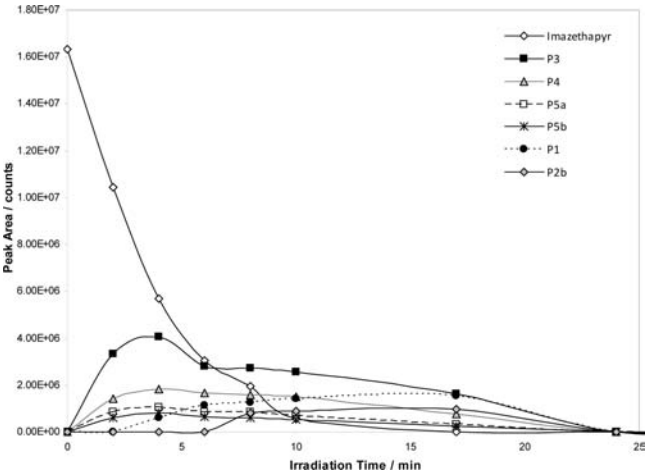

Figure 7. Evolution of imazethapyr degradation and photoproducts in pH 7.0 phosphate buffer with 253.7 nm light.

Table 3. Photoproducts of 5.12×10^{-5} M Imazethapyr Detected by LC-MS-ESI in Positive Mode in the Sample Irradiated under 253.7 nm Lamps for 6 min

peak	t_R (min)	$[M + H]^+$
P_1	5.00	203.2
P_2	5.46	218.2
P_3	5.83	247.1
P_4	6.21	262.2
P_{5a}	6.52	179.6
P_{5b}	6.52	194.1
imazethapyr	9.24	290.2

irradiation (after 6 min) but degrades by 24 min of irradiation. Therefore, after 24 min of irradiation, there are no measurable compounds in the solution.

The extracted ion chromatograms of each peak in the LC-MS chromatograms were obtained and compared with a blank sample. Each photoproduct produced an $[M + H]^+$ species in the positive ion mode, as shown in Table 3. When the extracted ion chromatograms of the peaks at 6.52 min were obtained, peaks corresponding to two masses appear in the chromatogram. On the basis of the data obtained by LC-MS analysis, we were unable to get a clear view of the structures of the photoproducts. For further characterization, peaks 3−6 were isolated and samples were taken to the University of Minnesota for analysis on a Bruker micrOTOF-Q, an instrument with 15000 mass resolution (fwhm) and high mass accuracy to 3 ppm. Accurate masses from this analysis, along with calculated empirical formulas and errors, are presented in Table 4. In addition, LC-ESI-MS-MS experiments were used to identify structures for the photoproducts and elucidate a possible photodegradation mechanism.

There have been several examinations of photoproduct formation for other imidiazolinone herbicides in the literature.[17,34−37] The difference in these herbicides is the substitution on the pyridine ring. In imazethapyr, the substituent is an ethyl group. Over the course of the irradiation and photoproduct formation, this substituent group and the pyridine ring itself are unchanged. This is also observed in the literature for imazamox,[34,38] imazapyr,[35,37] and imazapic.[17] Thus,

Table 4. Analysis Obtained from TOF-MS for Selected Photoproducts Formed upon Irradiation of 5.12×10^{-5} M Imazethapyr in pH 7.0 Phosphate Buffer[a]

peak	~m/z	measured mass	calculated mass	error (ppm)	formula $[M + H]^+$
P_{5a}	180	180.067(2)	180.0655	9	$C_9H_{10}NO_3$
P_{5b}	194	194.080(8)	194.0924	−60	$C_9H_{11}N_3O_2$
P_3	247	247.143(0)	247.1446	−6	$C_{14}H_{19}N_2O_2$
P_4	262	262.153(2)	262.1550	−7	$C_{14}H_{20}N_3O_2$
imazethapyr	290	290.148(7)	290.1499	−3	$C_{15}H_{20}N_3O_3$

[a] The measured masses are averages over several MS scans; the fourth decimal place for these averages is given in parentheses.

direct comparisons can be made between our data and the proposed mechanisms in the literature.

Because the photoproducts, P_3, P_4, and $P_{5a/b}$, all appear after 30 s of irradiation, we believe that there are several competing mechanisms occurring during the irradiation. Figure 9 illustrates the proposed mechanism. In general, the transformation appears to occur by the replacement of the carboxylic acid group and the rupture of C−N and C−O bonds in the imidazole moiety, as observed for other imidazolinones.[17,34−37]

Pathway A. The ion at m/z 262.153 corresponds to photoproduct P_4 with the formula $C_{14}H_{19}N_3O_2$. This product forms from the loss of C═O. Similar pathways of degradation have been observed for imazamox[34] and imazapyr;[35] however, the exact structure of the photoproduct has been debated. The C═O could be lost from the carboxylic acid group on the pyridine moiety to give a structure similar to I_5 in Harir et al.[34] or to the opening of the imidazolinone ring and the loss of the lactam C═O to give the structure given in Figure 9. Both of these structures have the same empirical formula and are possible products. Our tandem MS data indicate that the latter scenario is more likely, because fragmentation ions are observed with intact carboxylic acid groups (Figure 8a). We were unable to isolate photoproduct P_2 for examination with TOF-MS, but we know the m/z ratio (218.1) to four significant figures. A likely empirical formula for this product is $C_{13}H_{18}N_3$, and a possible structure is given in Figure 9. According to the related structures and the kinetic data, we believe that photoproduct P_2 is a decarboxylation product of P_4.

Pathway B. Photoproduct P_3 ($C_{14}H_{18}N_2O_2$, corresponding m/z 247.143) forms from the loss of H_2NC═O, most likely from the transposition reaction of a proton in the α-position of the imidazole ring. This pathway has also been observed for other imidazolinone herbicides.[17,34,36,37] Unlike the proposed mechanisms published by Quivet et al. for imazapyr[37] and imazamox,[36] in which the equivalent of product P_3 is formed from the equivalent of product P_4, we believe P_3 and P_4 are formed by separate, competing pathways. This conclusion is based on the fact that both of these products form at the same time during the irradiation; this conclusion is also supported by the mechanism proposed by Harir et al. for the degradation of imazamox.[34] Photoproduct P_1 (m/z = 203.2) was not isolated for exact mass analysis, but we believe the empirical formula to be $C_{13}H_{18}N_2$. The MS-MS data strongly support the structure proposed in Figure 9, with the primary fragments appearing as neutral losses of an allyl group and an azirine group. Given the late appearance in the irradiated solutions, P_1 could potentially be a degradation product of P_2 and/or P_3, as shown in Figure 9.

Pathway C. The TOF-MS data on P_{5b} gave an m/z ratio of 194.081; a logical empirical formula with a close m/z ratio is $C_{10}H_{11}NO_3$. This is the formula that was predicted by the TOF

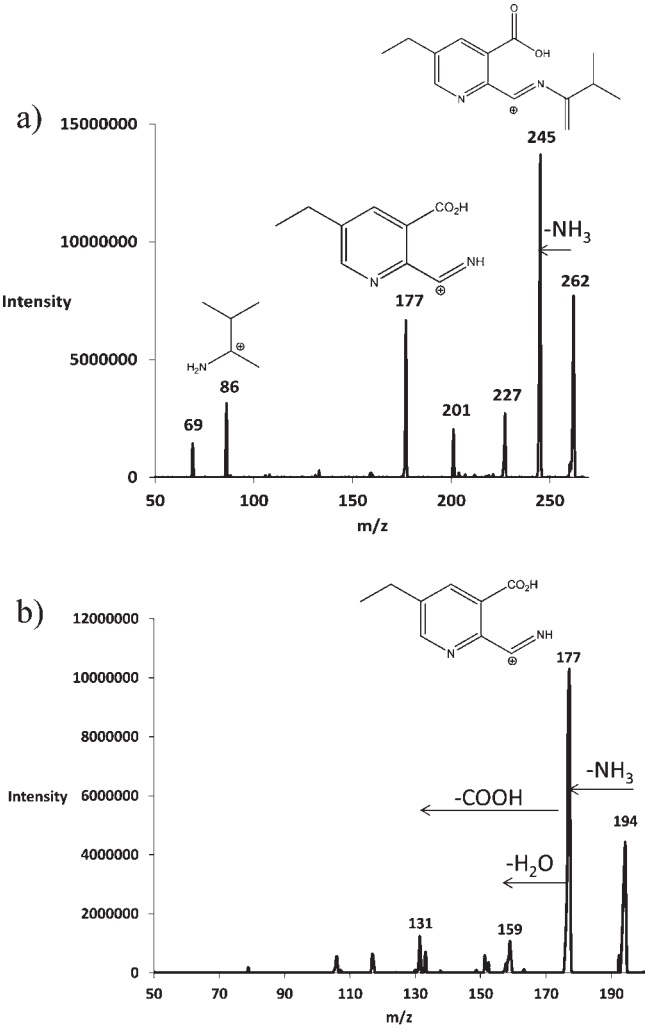

Figure 8. (a) Tandem mass spectrometry of photoproduct P_4 as an $[M + H]^+$ ion (m/z 262) in positive ion mode. (b) Tandem mass spectrometry of photoproduct P_{5b} as an $[M + H]^+$ ion (m/z 194) in positive ion mode.

MS software with an error of 9 ppm. However, our MS-MS data (Figure 8b) and the literature support the formula $C_9H_{11}N_3O_2$ (calculated mass of $[M + H]^+$ 194.0924). A possible structure for this compound is given in Figure 9. The only literature paper on the photolysis of an imidazolinone herbicide detecting the equivalent of $C_{10}H_{11}NO_3$ is a study by Harir et al. on imazapic.[17] However, although the authors report the related formula from their FTICR-MS data[17] (Table 3, peak 2c), the structure given in their proposed mechanism has a different formula[17]

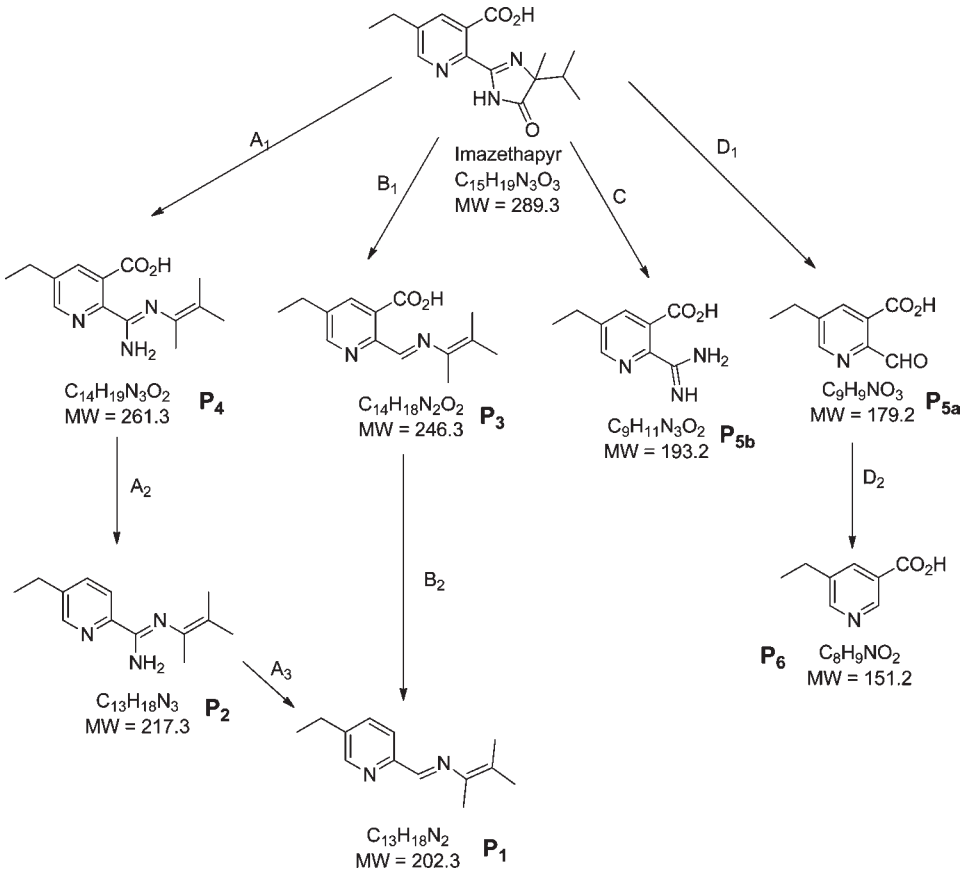

Figure 9. Proposed mechanistic pathways for the photolysis of imazethapyr at 253.7 nm.

(Figure 10, peak 2c). The formula corresponding to the one in Figure 10 of Harir et al. for imazethapyr degradation would be $C_9H_{11}N_3O_2$; the equivalents to this empirical formula have also been reported in the literature for several other imidazolinone herbicides.[34,37]

Pathway D. The final pathway observed for the photodegradation of imazethapyr involves the removal of the entire imidazole moiety with replacement by an aldehyde (P_{5a}, $C_9H_{10}NO_3$, corresponding m/z 180.067) and eventual removal of the aldehyde (P_6, m/z 152.1, $C_8H_9NO_2$). P_{5a} was analyzed with TOF-MS, but P_6, which appears only in samples irradiated for times >6 min, was not in the samples analyzed with TOF-MS (that sample was only irradiated for 6 min). However, we know the m/z ratio to four significant figures and observe the product only at later irradiation times (after P_{5a} begins to disappear). This pathway is also supported by the literature.[34]

The proposed photodegradation mechanism for imazethapyr at 253.7 nm (Figure 9) supports aspects of photodegradation mechanisms given for other imidazolinone herbicides[17,34,35,37] despite the difference in irradiation wavelength (the wavelengths used in the literature were all >290 nm). Therefore, although this study was conducted at a wavelength that is not environmentally relevant, the similarities in observed photoproducts to experiments with other imidazolinone herbicides at environmentally relevant wavelengths (i.e., >290 nm) suggest that imazethapyr degradation in the environment may be similar in mechanism to the one presented here. However, it is anticipated that the degradation would be slower in the environment due to higher wavelengths, lower intensities of light, and the presence of natural organic matter.

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