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Analysis of the Photodegradation of the Imidazolinone Herbicides Imazamox, Imazapic, Imazaquin, and Imazamethabenz-methyl in Aqueous Solution

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Supporting Information

ABSTRACT: The photodegradation of the imidazolinone herbicides imazamox, imazapic, imazaquin, and imazamethabenz-methyl has been investigated in phosphate-buffered solutions and buffered solutions containing natural organic matter (NOM). The hydrolysis of imazamethabenz-methyl, the only imidazolinone herbicide susceptible to hydrolysis, was also examined. The rate of hydrolysis of imazamethabenz-methyl increased with increasing pH, with the *para* isomer degrading more rapidly than the *meta* isomer. All photodegradation rate constants increased with pH and plateaued after pH 5.2. All imidzaolinones degraded more quickly under 253.7 nm lamps as compared to degradation under 310 nm lamps. Imazamox and imazapic degraded more rapidly than imazaquin at all pH values and had higher quantum yields. In addition, imazamox and imazapic quantum yields increased as a function of pH, whereas imazaquin quantum yields showed no trend as a function of pH. Photodegradation reaction rate constants decreased as the concentration of NOM was increased in the solutions due to the effect of light screening. Formulas for the proposed photoproducts for imazamox, imazapic, and imazaquin in pH 7 phosphate buffers were identified, and structures for the photoproducts are proposed.

KEYWORDS: *imidazolinones, natural organic matter, hydrolysis, photodegradation, photoproducts*

INTRODUCTION

Imidazolinone herbicides have been used to control broadleaf and grassy weeds in alfalfa, peanuts, imidazolinone-tolerant maize, oilseed rape, rice, wheat, and sunflowers since the 1980s.[1] These herbicides work by inhibiting the enzyme acetohydroxyacid synthase, which is responsible for the synthesis of branched-chain amino acids in plants.[2] Commercial herbicide products such as Beyond, Cadre, Image, and Assert contain the imidazolinone active ingredients imazamox (2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methoxymethyl-nicotinic acid), imazapic (5-methyl-2-[4-methyl-5-oxo-4-(propan-2-yl)-4,5-dihydro-1*H*-imidazol-2-yl]pyridine-3-carboxylic acid), imazaquin (2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-yl)-3-quinolinecarboxylic acid), and imazamethabenz-methyl (methyl 6-(4-isoporpyl-4-methyl-5-oxo-2-imidazolin-4-yl)-*p*-toluate and *m*-toluate), respectively, as active ingredients (all shown in Figure 1).[3,4] These herbicides all exhibit low mammalian toxicity.[1] However, their effects on other ecosystems are considerably less harmless. Imidazolinones have been shown to adversely affect nontarget terrestrial and aquatic vascular plants, including some endangered species. Nonlethal contact with the herbicides was shown to induce chlorosis, necrosis, and stunting in nontarget plants, emphasizing the relevance of studying these herbicides in water.[5]

The protonation states of these herbicides are important to the compounds' sorption on soils and their abiotic degradation.[6] These herbicides are all weak organic acids (imazamox,[7] pK_{a1} = 2.3, pK_{a2} = 3.2, pK_{a3} = 10.6; imazapic, pK_{a1} = 2, pK_{a2} = 3.6, pK_{a3} = 11.1; imazaquin,[8,9] pK_{a1} = 1.8, pK_{a2} = 3.8, pK_{a3} = 11.0;[10] imazamethabenz-methyl,[11] pK_{a1} = 3.4, pK_{a2} = 9.4).

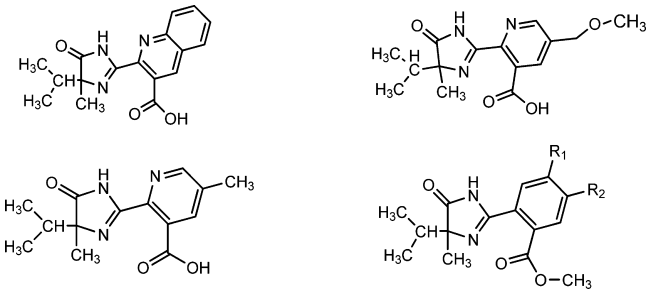

Figure 1. Structures of imidazolinone herbicides: (top left) imazaquin (IMZQ); (top right) imazamox (IMZX); (bottom left) imazapic (IMZP); (bottom right) imazamethabenz-methyl (IMZB); for *p*-IMZB, R_1 = CH_3 and R_2 = H; for *m*-IMZB, R_1 = H and R_2 = CH_3.

Imazamox, imazapic, and imazaquin all have three protonation states; the first state is protonation of the nitrogen in the imidazole ring (=N−), the second is ionization of the carboxylic acid, and the third is deprotonation of the NH group in the imidazole ring. The dissociation of imazamox, imazapic, and imazaquin is shown in Figure 2a. Although Figure 2a shows the neutral species without charges, there is some discussion in the literature that this may actually exist as a zwitterion (with a negative charge on the carboxylic and positive charge on a protonated =N− in the imidazole

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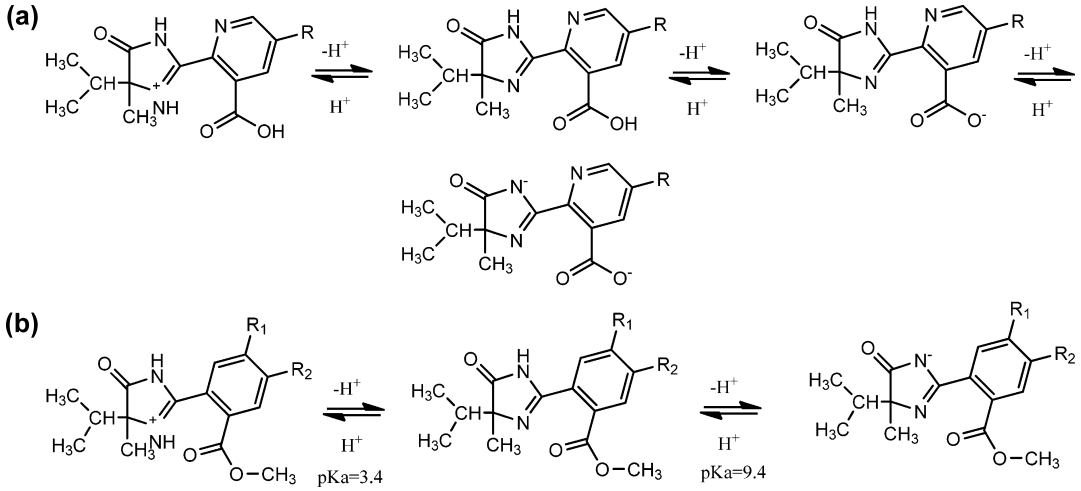

Figure 2. (a) Dissociation of imidazolinone herbicides imazamox (IMZX), imazapic (IMZP), and imazaquin (IMZQ). R = O−CH_3 for IMZX and R = CH_3 for IMZP. Similar structures can be drawn for IMZQ with a quinolone ring instead of the pyridine ring. (b) Dissociation−protonation of imazamethabenz-methyl (IMZB).

ring).[10,12] Figure 2b shows the dissociation pattern for imazamethabenz-methyl. It is important to note the differences in the structure of imazamethabenz-methyl when compared to the other herbicides studied. Instead of a pyridine ring and a carboxylic acid, imazamethabenz-methyl contains a benzene ring and an ester. Thus, imazamethabenz-methyl has only two pK_a values—one for the protonation of the double-bonded nitrogen in the imidazole ring and the other for the deprotonation of the NH group in the imidazole ring. Additionally, imazamethabenz-methyl is the only herbicide studied with two isomers, *para* and *meta*. Imazamethabenz-methyl is of neutral charge at neutral pH, whereas the other herbicides studied are anionic at neutral pH. This likely affects the sorption and degradation of imazamethabenz-methyl.

The high water solubility and anionic structures of imazamox, imazapic, and imazaquin at neutral pH values contribute to their high mobility in soils and water.[6] Because these herbicides have found widespread use in the Midwestern portion of the United States (ranging from 0.0028 to 1.2929 lb/mi^2), it is of interest to study the fate of these compounds in water samples.[13−16] Although the effects these herbicides have on the environment are not completely known, controlled experiments in a laboratory setting can be used to simulate environmental processes, such as photolytic degradation, to aid in forming hypotheses about the fate of these herbicides in aquatic systems.

After a herbicide has been applied to crops and is washed away through runoff, it can be transformed through biotic and abiotic pathways induced by sunlight, heat, radicals, organics, microorganisms, or other factors.[6] One of the most important pathways for degradation of imidazolinones in aqueous systems is photolysis, as was found by Ramezani et al.[17]

The photodegradation of imidazolinone herbicides has been the subject of several studies.[2,17−23] The most extensive study of imazaquin to date was conducted by Barkani et al., in which the effects of pH, wavelength, and oxygen concentration on the rate of photodegradation were examined, and five photoproducts and a mechanism of degradation were proposed.[23] With regard to imazapic, the most extensive study was conducted by Harir et al., in which the effects of imazapic concentration, pH, and temperature were examined.[2] Photoproducts were also separated, and a mechanistic pathway was proposed.[2] Imazamox has been less extensively studied, as only the effects of ultraviolet light have been examined, and a few photoproducts have been identified.[18] The least studied of the herbicides examined in this work is imazamethabenz-methyl, as only the hydrolysis and photoproducts of this herbicide have been studied, with no systematic study of the impact of water quality on photolysis.[20,22] Although photodegradation has been studied frequently, none of these studies has combined the same parameters as the present work or sought to compare these herbicides to one another. Despite previous investigations, more work is needed to understand the photodegradation, occurrence, long-term fate, and water transport of these herbicides in surface water and groundwater.

In this paper, the photolysis reactions of the herbicides imazamox, imazapic, imazaquin, and imazamethabenz-methyl as functions of wavelength, pH, and natural organic matter (a model for river systems) have been studied, as well as the hydrolysis of imazamethabenz-methyl. The quantum yields for the photolysis of each imidazolinone irradiated with 310 nm mercury lamps have been calculated as a function of pH; these include quantum yields that have not been determined by previous researchers. In addition, the major photoproducts in these systems have been proposed.

MATERIALS AND METHODS

Chemicals and Instrumentation. Imazamox (purity = 99.5%), imazapic (purity = 98.7%), imazaquin (purity = 99.5%), and imazamethabenz-methyl (purity = 97.4%) were purchased from ChemService or Sigma-Aldrich and used as received. Acetonitrile (ACN), >99.9% (HPLC grade), was purchased from Sigma-Aldrich. Ten millimolar phosphate buffers were prepared using combinations of H_3PO_4, $NaH_2PO_4{\cdot}H_2O$, and $Na_2HPO_4{\cdot}7H_2O$ (all purchased from Fisher Scientific) as needed in Milli-Q water. All natural organic matter (NOM) was obtained from the International Humic Substance Society (IHSS) collected from the Suwannee River (1R101N). Actinometry was performed using *p*-nitroacetophenone (PNAP − 98%) obtained from Aldrich.

HPLC analysis was performed with a Hewlett-Packard 1090 liquid chromatograph. The column used was an Agilent Zorbax C18 reverse-phase column with 10 cm × 4.6 mm dimensions and 3.5 μm particle size. The methods used for each herbicide are as follows: in all methods, the injection volumes were 10 μL, the oven was set at 36 °C (except for imazamethabenz-methyl, which had an oven temperature of 40 °C), and the detection wavelength was 220 nm. For imazapic

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samples at pH 3 and 5, the isocratic mobile phase consisted of 50% ACN and 50% 1.7 mF aqueous phosphoric acid buffer (pH ~3) with a flow rate of 0.4 mL/min and a 5 min run time. Imazapic samples at pH 7 had an isocratic mobile phase of 20% ACN and 80% aqueous 1.7 mF phosphoric acid buffer (pH ~3) with a flow rate of 0.75 mL/min and an 8 min run time. For imazaquin, the isocratic mobile phase consisted of 60% ACN and 40% aqueous 1.7 mF phosphoric acid buffer (pH ~3) with a flow rate of 0.5 mL/min and a 5 min run time. At pH 3, the method used for imazamox had an isocratic mobile phase consisting of 50% ACN and 50% aqueous 1.7 mF phosphoric acid buffer (pH ~3) with a flow rate of 0.4 mL/min and a 5 min run time. At pH 5 and 7, the imazamox method had an isocratic mobile phase consisting of 30% ACN and 70% aqueous 1.7 mF phosphoric acid buffer (pH ~3) with a flow rate of 0.75 mL/min and a 5 min run time. For all imazamethabenz-methyl samples, the isocratic mobile phase was 30% ACN and 70% aqueous 1.7 mF phosphoric acid buffer (pH ~3) with a flow rate of 1.5 mL/min and a 5 min run time. The optimized HPLC method for PNAP also used the Hewlett-Packard 1090 liquid chromatograph with the Agilent Zorbax C18 reverse-phase column described above. The injection volume was changed to 8 μL, but the oven remained set at 36 °C. The isocratic mobile phase consisted of 30% ACN and 70% pH 5.3 acetate buffer with a flow rate of 0.5 mL/min and a 10 min run time. The detector was set at 288 nm.

Hydrolysis in Buffered Solution. Samples of imazamethabenz-methyl buffered at pH 7.99 (5.2×10^{-5} M) and pH 9.05 (5.9×10^{-5} M) were placed in 40 mL amber vials in a heated water bath at 24 °C. At predetermined time points, an aliquot (~1.0 mL) of each sample was removed and analyzed in triplicate via HPLC against a set of imazamethabenz-methyl standards. Samples of imazamethabenz-methyl buffered at pH ~9.4 were placed in amber HPLC vials and set inside the HPLC oven to maintain a controlled temperature. At predetermined time points, samples were analyzed in triplicate via HPLC against a set of imazamethabenz-methyl standards. Two experiments were conducted at the highest pH with initial imazamethabenz-methyl concentrations of 5.2×10^{-5} and 5.5×10^{-5} M.

Photolysis Using Artificial Light. Solutions of the four herbicides (imazamox, imazapic, imazaquin, and imazamethabenz-methyl) were prepared at 15 mg/L concentrations (i.e., 4.9×10^{-5} M imazamox, 5.4×10^{-5} M imazapic, 4.8×10^{-5} M imazaquin, and 5.2×10^{-5} M imazamethabenz-methyl) at different pH values (1, 3, 5, 7, and 9). The solutions were prepared by dissolving 7.5 mg in 500 mL of the appropriate-pH phosphate buffers. The dissolution was aided through sonication for 5 min. When needed, solutions of herbicide with 1.0–10.0 mg/L NOM were prepared in pH 7 phosphate buffer.

These solutions were used for two different trials, one with exposure to 253.7 nm light and the other to 310 nm light. Ten milliliter aliquots of a solution were placed into 26 quartz test tubes and distributed evenly within a merry-go-round Rayonet RPR-100 photochemical reactor (Southern New England Ultraviolet Co.). The Rayonet contained eight 35 W low-pressure mercury lamps that emitted light centered at 253.7 or 310 nm. The 253.7 nm lamps are line spectra lamps, whereas the 310 nm lamps have a broad spectral distribution with a full width at half-maximum of 40 nm. Thirteen test tubes were exposed to 253.7 nm light, and 13 were exposed to 310 nm light for time intervals of ≤20 min. These samples were then collected for analysis by HPLC.

Photon Flux and Quantum Yield Experiments. The *p*-nitroacetophenone (PNAP) actinometer was used to determine the quantum yield of imazamox, imazapic, and imazaquin irradiated with the 310 nm lamps in the RPR-100 photochemical reactor. The quantum yield of PNAP depends on the concentration of pyridine through the following relationship (taken from Leifer, eq 6.12[24]):

$$\varphi_{PNAP} = 0.0169[Pyr] \quad (1)$$

This equation shows that to increase the photodegradation rate of PNAP, the concentration of pyridine needs to be increased (as long as the concentration of pyridine remains below 0.2 M).[24] A solution of 6.48×10^{-5} M PNAP and 0.198 M pyridine was irradiated in the RPR-100 to determine the rate constant of photodegradation. Because the rate constant was only slightly slower than that of the imidazolinone herbicides under the same conditions, this solution was used for subsequent actinometer experiments with the RPR-100. Determination of the quantum yields is described in detail below.

Preparation and Analysis of Photoproducts. Imazamox, imazapic, imazaquin, and imazamethybenz-methyl samples were irradiated with eight 310 nm lamps in the RPR-100 for times of 0, 16, 30, and 60 min. Analysis on the UHPLC/MS was performed for the determination of photoproducts. UHPLC/MS for separation and accurate mass analysis of the compounds studied here was carried out with an Agilent Infinity UHPLC coupled to an Agilent 6230 TOF mass spectrometer. LC separations were made using a 2.1 mm × 100 mm Agilent EC-C18 (2.7 μm particle size) reversed-phase chromatography column (Agilent Technologies) at 35 °C. The mobile phase consisted of (A) water (obtained from a house Milli-Q purification system (Billerica, MA, USA)) containing 0.1% formic acid (Sigma-Aldrich, St. Louis, MO, USA) or (B) acetonitrile (Sigma-Aldrich ChromaSolv LC/MS-grade). Compounds were eluted using the following gradient elution conditions at a flow rate of 0.25 mL/min: 5–40–100–100–5–5% B from 0 to 10–12–13–13.01–15 min, and the sample injection volume was 10 μL. The TOF mass spectrometer was configured with a Dual Agilent JetStream electrospray ionization source, using HP-0921 (hexakis(1*H*,1*H*,3*H*-tetrafluoropropoxy)phosphazine; exact mass, 922.00978 Da; Agilent Technologies) as a reference mass for within-run mass calibration. EMass spectra were acquired over the range m/z 100–3000 every 1 s during the chromatographic separations. Other mass spectrometer conditions were as follows: capillary voltage, 3.5 kV; nozzle voltage, 1.0 kV; fragmentor voltage, 155 V; source temperature and gas flow, 250 °C and 6 L/min, respectively; nebulizer pressure, 50 psi nitrogen; sheath gas temperature and flow, 250 °C and 11 L/min, respectively.

Computational Analysis of Photoproducts. Gaussian 03 with Web-MO interface was used for computational analysis. Reactant and product, including the CO bond, geometry optimizations, and thermochemical analysis, were calculated at the B3LYP/cc-PVDZ level. Transitions states were identified using the QST3 method.

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 herbicide 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.[25] The use of this weight reduces the effect of the later time on the fit of the regression line, yielding more accurate reaction rate constants. Rate constants given in the text and tables are listed as experimental value plus/minus the standard deviation.

RESULTS AND DISCUSSION

Imazamethabenz-methyl Hydrolysis and Photolysis. The first challenge in examining the hydrolysis and photolysis of the two isomers of imazamethabenz-methyl was separating and identifying them on the HPLC. After method development, the final HPLC method above separated the two isomers with a resolution of R_s = 1.8. One isomer eluted with a retention time of 2.110 min, and the other had a retention time of 2.169 min (see the Supporting Information). The water solubility of the *para* isomer is 857 g/L, whereas the water solubility of the *meta* isomer is 1370 g/L.[26] With a reverse-phase column, these water solubilities suggest that the *meta* isomer is the one with the earlier retention time. In addition, the literature states that the ratio of *para* to *meta* isomers in the synthesis of imazamethabenz-methyl should be roughly 60% *para* to 40% *meta*.[9,22] The ratio of the two isomers in the chromatographs (see the Supporting Information) was 64% to 36%. Both the water solubility and synthesis information support the *meta* isomer as eluting first from the column. The opposite elution sequence was observed by Brigante et al.,[22]

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Table 1. Observed Hydrolysis Rate Constants, k_{app}, for Two Imazamethabenz-methyl Isomers from This Study and Brigante et al.[22]

		this study		Brigante et al.	
temp (°C)	pH	k_{meta} (h^{-1})	k_{para} (h^{-1})	k_{meta} (h^{-1})	k_{para} (h^{-1})
24	8.0[a]	0.0023 ± 0.0003	0.0014 ± 0.0003	0.0028	0.001
24	9.1[a]	0.016 ± 0.002	0.009 ± 0.001	0.0152	0.0077
24	9.4[b]	0.050 ± 0.006	0.028 ± 0.003		
31	9.1[a]	0.020 ± 0.002	0.009 ± 0.001		
43	9.1[a]	0.128 ± 0.02	0.066 ± 0.008		

[a]Only one experiment was completed; error bars represent 12% of the average (the relative standard deviation from the pH 10 experiments). [b]An average of two experiments was used to determine the rate constants and error bars (reported as one standard deviation).

perhaps due to slightly different column chemistries in the HPLC.

Hydrolysis experiments were conducted in the dark at 24 °C at pH values of 8.0, 9.1, and 9.4. Hydrolysis followed pseudo-first-order kinetics at all pH values. Table 1 presents the hydrolysis rate constants. Rate constants increase with more alkaline conditions, which corresponds to studies by Brigante et al.[22] The *para* isomer always degrades more rapidly than the *meta* isomer at the same observed pH values. The apparent kinetic order was found using the expression

$$r = k_{app}[\text{IMZB}] \tag{2}$$

where r is the hydrolysis degradation rate and k_{app} is the apparent kinetic constant. This constant can be established using the expression

$$k_{app} = k_A[H^+]^a + k_B[OH^-]^b + k_N \tag{3}$$

where k_A, k_B, and k_N represent the kinetics constants for the acidic, basic, and neutral forms, respectively. a and b represent the kinetic orders toward proton and hydroxide ions. Because this study was conducted at basic pH, k_A and k_N are very small compared to k_B and can be neglected. Therefore, the expression for k_{app} can be rewritten as $k_{app} = k_B[OH^-]^b$ or

$$\log k_{app} = \log k_B + b \log[OH^-] \tag{4}$$

In the paper published by Brigante et al., K_w was assumed to be 14 when $[OH^-]$ was converted to $[H^+]$.[22] However, because K_w is dependent upon temperature, a correction must be made to the K_w value using eq 5:[27]

$$\log K_w = -\frac{4470.99}{T} + 6.0875 - 0.01706T \tag{5}$$

With these corrections, $\log(K_w)$ is 14.03 in our experiments (at T = 24 °C) and the $\log(K_w)$ value is 14.17 for Brigante et al. (20 °C). Using eq 4, values for $\log k_{app}$ were plotted against $\log[OH^-]$ values to determine $\log k_B$ and b, the order with respect to $[OH^-]$ (see the Supporting Information for the plot). Table 2 presents the k_B and b values that were found for the *para* and *meta* isomers in both studies. For this study, the order of reaction for the *para* isomer was determined to be 0.89, and for the *meta* isomer it was found to be 0.93; we confirm that the apparent kinetic order of hydrolysis is close to one against hydroxide ions. This coincides with data from Brigante et al.; with the corrections due to the temperature dependence of $\log(K_w)$, their values were 0.85 for the *para* isomer and 0.71 for the *meta* isomer. In addition, Table 2 shows (1) using the correct value of K_w with the data reported in Brigante et al. increases their values of k_B by roughly 30% and (2) the k_B values determined in our experiments are higher than

Table 2. Base Hydrolysis Rate Constants, k_B, and the Order of Reaction with Respect to $[OH^-]$, b, for Two Imazamethabenz-methyl Isomers from This Study and Brigante et al.[22]

	this study		Brigante et al.	
	k_B (h^{-1})	b	k_B (h^{-1})	b
m-IMZB	908	0.93	103[a]	0.71
p-IMZB	296	0.89	260[b]	0.85

[a]The value from Brigante et al. was 78 h^{-1}. The adjustment above is from the correction to K_w as a function of temperature. [b]The value from Brigante et al. was 186 h^{-1}. The adjustment above is from the correction to K_w as a function of temperature.

the corrected values based on the Brigante et al. work. For the *meta* isomer, the k_B value obtained in this study is 7 times larger than that obtained by Brigante et al., corresponding to the larger observed rate constants. The difference is smaller for the *para* isomer; the k_B values are on the same order for both studies. It remains unclear why the *meta* isomer is degrading so much more quickly in the current study relative to the work of Brigante et al.

To determine the pre-exponential factor, A, and activation energy, E_a, of imazamethabenz-methyl hydrolysis, experiments were conducted with pH 9.1 solutions at 24, 31, and 43 °C. The rate constants for these experiments are included in Table 2. Regression of $\ln(k_{app})$ versus $1/T$ according to the Arrhenius equation

$$\ln k_{app} = \ln A - \frac{E_a}{RT} \tag{6}$$

gives $A = 4.73 \times 10^{14}$ M^{-1} s^{-1} and E_a = 94.5 kJ mol^{-1} for the *para* isomer. For the *meta* isomer, $A = 3.74 \times 10^{14}$ M^{-1} s^{-1} and E_a = 95.8 kJ mol^{-1}. The difference in reaction rates for these isomers is therefore due to the Arrhenius factor, not the activation energy, suggesting that the sterics and orientation of the two isomers are more important in hydrolysis than energetics. The activation energies of these two isomers are of the same magnitude found for the hydrolysis of other herbicides.[28−31]

Direct photolysis experiments of imazamethabenz-methyl were conducted under acidic and neutral pH values to prevent hydrolysis. All photolysis experiments demonstrated pseudo-first-order kinetics. Table 3 provides the kinetic rate constants for both isomers when irradiated at 253.7 and 310 nm. As illustrated by the table, the rate constants increased with increasing pH up to a pH of 5.2 and the rate constants at pH 5.2 and 7.0 were statistically equivalent. This trend is due to the presence of the different species of imazamethabenz-methyl at different pH values (see Figure 2b). At pH 1.44, 99% of the

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Table 3. Rate Constants and Quantum Yields for Imazaquin, Imazamox, Imazapic, and Two Imazamethabenz-methyl Isomers When Irradiated at 253.7 and 310 nm

compound	pH	k_{254} (min^{-1})	k_{310} (min^{-1})	φ_{310}
imazaquin	0.92	0.10 ± 0.02	0.014 ± 0.001	0.009
	3.07	0.16 ± 0.05	0.08 ± 0.02	0.068
	5.33	0.20 ± 0.02	0.129 ± 0.003	0.037
	6.90	0.25 ± 0.00[a]	0.18 ± 0.01	0.074
	8.73	0.238 ± 0.003	0.167± 0.001	0.035
imazamox	0.92	0.18 ± 0.04	0.03 ± 0.01	0.035
	3.08	0.12 ± 0.03	0.09 ± 0.01	0.044
	5.32	0.30 ± 0.05	0.207 ± 0.002	0.133
	6.90	0.30 ± 0.02	0.22 ± 0.02	0.176
	8.73	0.29 ± 0.01	0.20 ± 0.01	0.123
imazapic	0.92	0.18 ± 0.01	0.036 ± 0.001	0.061
	3.06	0.12 ± 0.02	0.07 ± 0.02	0.036
	5.32	0.29 ± 0.03	0.193 ± 0.003	0.187
	6.90	0.30 ± 0.01	0.21 ± 0.01	0.205
	8.73	0.35 ± 0.02	0.21 ± 0.01	0.127
imazamethabenz-methyl, *meta* isomer	1.44	0.070[b]	0.016[b]	[c]
	3.29	0.28 ± 0.02	0.096 ± 0.001	[c]
	5.20	0.42 ± 0.03	0.148 ± 0.002	[c]
	7.02	0.38 ± 0.04	0.16 ± 0.01	[c]
imazamethabenz-methyl, *para* isomer	1.44	0.082[b]	0.008[b]	[c]
	3.29	0.35 ± 0.02	0.08 ± 0.01	[c]
	5.20	0.4 ± 0.1	0.11 ± 0.01	[c]
	7.02	0.42 ± 0.03	0.12 ± 0.01	[c]

[a]The two rate constants determined at these conditions were the same so the standard deviation is calculated to be zero. [b]There was only one rate constant taken at this pH so no error bars can be calculated. [c]The quantum yield was not determined for each isomer because they were not separated for UV/vis analysis.

imazamethabenz-methyl is in the cationic form; by pH 3.29, only 56% is in the cationic form. At pH 5.2 and 7, roughly 99% of the imazamethabenz-methyl is in the neutral form. The rate constants in Table 3 show that the cationic form is less susceptible to photolysis than the neutral form. Brigante et al. also saw this relationship between pH and reaction rate for imazamethabenz-methyl.[22]

Table 3 also allows a comparison of the photolysis rates for the two isomers of imazamethabenz-methyl (IMZB). At 310 nm, the *meta* isomer is more reactive than the *para* isomer (e.g., at pH 7.02, $t_{1/2}$ of *m*-IMZB is 4.3 min and $t_{1/2}$ of *p*-IMZB is 5.8 min). This supports the results of Brigante et al.[22] The wavelength of irradiation also has an effect on the photolysis rate constants. In general, the rate constants at 253.7 nm are faster than those at 310 nm as expected due to the higher absorption of imazamethabenz-methyl at 253.7 nm and the more energetic photons at that wavelength. More interesting is the observation that at 253.7 nm, the difference between the isomers' rate constants is much smaller (e.g., at pH 7.02, $t_{1/2}$ of *m*-IMZB is 1.8 min and $t_{1/2}$ of *p*-IMZB is 1.7 min). In fact, at the lower pH values, the data suggest the *para* isomer is slightly more reactive than the *meta* isomer when irradiated at 253.7 nm (e.g., at pH 3.29, $t_{1/2}$ of *m*-IMZB is 2.5 min and $t_{1/2}$ of *p*-IMZB is 2.0 min).

Wavelength- and pH-Dependent Direct Photolysis of Imazamox, Imazapic, and Imazaquin. As with imazamethabenz-methyl, all photolysis experiments with imazamox, imazapic, and imzaquin showed an exponential decay of the compound concentration with time, suggesting a first-order or pseudo-first-order reaction. Rate constants were determined by applying first-order kinetic models to the data. Table 3 presents the rate constants for all of the compounds as a function of wavelength of light used for irradiation and the pH of the solution. As seen in Table 3, the rate constants for each compound irradiated with 253.7 nm light are faster than the corresponding rate constants with 310 nm light. Changes in degradation rates with the different lamps are due to differences in photon flux, energy of the photons, and molar absorptivities of the imidazolinones at the two wavelengths.

As discussed in the Introduction, all of these imidazolinone herbicides act as weak acids and exist as different species at various pH values. Because these compounds can exist in several protonation states, experiments were conducted in phosphate-buffered solutions with pH values ranging from 3 to 9. An additional set of experiments was conducted at pH 1 using 0.1010 M standardized HCl as the solvent. These experiments were conducted with both 253.7 and 310 nm lamps in the RPR-100. Table 3 summarizes the data from these experiments showing the rate constants increase with increasing pH, plateauing above a pH of 5. A graphic view of these results is presented in the Supporting Information (Figures S3−S5); the figures show the photodegradation rate constants with 253.7 and 310 nm lamps plotted as a function of pH overlaying the fractional amounts of each species. All graphs show the same pattern. Table 3 and Figure S3 show that the anionic form of imazamox is more reactive than the neutral form, which in turn is more reactive than the cationic form (i.e., anionic > neutral > cationic), which is also true for imazaquin and imazapic irradiated at 310 nm. However, when irradiated at 253.7 nm, the reaction rate constants for the cationic forms of imazamox and imazapic are larger than those of the neutral forms (i.e., anionic > cationic > neutral). When analyzing the photochemistry of imazaquin, Barkani et al. also observed that the photodegradation rate constant for the anionic form was greater than the neutral or cationic form.[23] Through the use of fluorescence spectroscopy, these authors showed that the carboxylic group was not directly involved in the photodegradation but that photodegradation was favored when the carboxylic group was in the anionic form.[21]

Table 3 also compares the photodegradation rate constants for imazamox, imazaquin, and imazapic at a series of pH values. Under both 253.7 and 310 nm lamps, imazaquin reacts more slowly than imazapic and imazamox at all pH values (with one exception at pH 3 with 253.7 nm light). The difference between these three imidazolinone herbicides is in the substituent on the pyridine ring. For imazamox, the substituent is a methyl ether and for imazapic, it is a methyl group. The aromatic ring in imazaquin causes the pyridine present in the other imidazolinone herbicides to become a quinolone moiety. Methyl ethers and methyl groups are electrodonating to the pyridine ring[32] and thereby reduce the stability of the carboxylic anion that is present at any pH above the pK_a of the carboxylic acid (approximately pH 4). Although the methyl ether should have a larger effect than the methyl group, the two are both weak electron-donating groups and the difference is somewhat minor. This is evident by the similar photodegradation rate constants of imazamox and imazapic above pH 4. On the other

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Table 4. Experimental (k_{obs}) and Light Screening Corrected (k_{corr}) Rate Constants for Irradiation of pH 7.0 4.8 × 10^{-5} M Imazaquin/NOM, 4.9 × 10^{-5} M Imazamox/NOM, and 5.4 × 10^{-5} M Imazapic/NOM Solutions at 253.7 and 310 nm

		253.7 nm			310 nm		
compound	[NOM] (mg/L)	k_{obs} (min^{-1})	$S(\lambda)$	k_{corr} (min^{-1})	k_{obs} (min^{-1})	$S(\lambda)$	k_{corr} (min^{-1})
imazaquin	0	0.25 ± 0.00[a]			0.18 ± 0.01		
	1	0.27 ± 0.02	0.91	0.30 ± 0.02	0.16 ± 0.03	0.98	0.16 ± 0.03
	5	0.22 ± 0.04	0.90	0.25 ± 0.04	0.13 ± 0.03	0.94	0.14 ± 0.03
	10	0.22 ± 0.06	0.81	0.27 ± 0.06	0.14 ± 0.01	0.90	0.16 ± 0.01
imazamox	0	0.30 ± 0.02			0.22 ± 0.02		
	1	0.33 ± 0.02	1.0	0.33 ± 0.02	0.20 ± 0.02	1.0	0.20 ± 0.02
	5	0.30 ± 0.02	0.88	0.34 ± 0.02	0.18 ± 0.03	0.95	0.19 ± 0.03
	10	0.25 ± 0.03	0.84	0.30 ± 0.03	0.15 ± 0.02	0.90	0.17 ± 0.03
imazapic	0	0.30 ± 0.01			0.21 ± 0.01		
	1	0.28 ± 0.08	0.89	0.31 ± 0.08	0.19 ± 0.02	0.98	0.19 ± 0.02
	5	0.28 ± 0.03	0.82	0.34 ± 0.03	0.20 ± 0.02	0.94	0.21 ± 0.02
	10	0.23 ± 0.07	0.77	0.30 ± 0.07	0.16 ± 0.03	0.90	0.18 ± 0.03

[a]The two rate constants determined at these conditions were the same so the standard deviation is calculated to be zero.

hand, the aromatic ring *meta* to the carboxylic group on imazaquin should have a slight electron-withdrawing effect and increase the stability of the carboxylic anion.[33] This explains the smaller photodegradation rate constants for imazaquin compared to imazamox and imazapic. Although this argument does not explain the lower rate constants for imzaquin at pH values below the pK_a of the carboxylic acid, it is likely that the difference in rate constants is due to the effect the subsistent groups on the pyridine ring have on the photodegradation mechanism.

Quantum Yields of Imazamox, Imazapic, and Imazaquin. Using chemical actinometry of the PNAP/PYR system, the quantum yields for imazamox, imazapic, and imazaquin under the 310 nm lamps in the RPR-100 were determined. As the 310 nm lamps model the solar spectrum, these quantum yields are environmentally relevant. The quantum yields of the imazamethabenz-methyl isomers were not determined as they were not physically separated, and collecting separate UV/vis spectra proved challenging. Quantum yields were determined at all pH values used in the photolysis studies (pH 1, 3, 5, 7, and 9). Because the 310 nm lamps are polychromatic, eq 7 (adapted from Leifer, eq 6.18[24]) was used to determine the quantum yields:

$$\phi_I = \frac{k_I}{k_{PNAP}} \left\{ \frac{\sum_\lambda \varepsilon_{\lambda,PNAP} L_\lambda}{\sum_\lambda \varepsilon_{\lambda,I} L_\lambda} \right\} \phi_{PNAP} \quad (7)$$

In eq 7, k_I and k_{PNAP} are the first-order reaction rate constants for an imidazolinone and PNAP, $\varepsilon_{\lambda I}$ and $\varepsilon_{\lambda PNAP}$ are the molar absorptivity (M^{-1} cm^{-1}) at each wavelength λ for the imidazolinone and PNAP, L_λ is the irradiance at wavelength λ (einstein cm^{-2} day^{-1}), and ϕ_{PNAP} is the quantum yield for PNAP. An ILT950 spectroradiometer from International Light Technologies was used to measure the irradiance of the lamps in the RPR-100. The quantum yield for PNAP was determined using eq 1 and was found to be 3.3 × 10^{-3}. Using these values in eq 7, the quantum yield for each imidazolinone at five different pH values was determined. The results of these calculations can be found in Table 3. As with the photodegradation rate constants, the quantum yields for imazamox and imazapic are greater than those for imazaquin. For imazamox and imazapic, the quantum yields increase as a function of pH, but start to decrease slightly at pH 8.96. The quantum yields for imazaquin follow no trends as a function of pH, which contradicts the trend observed by Barkani et al.[23]

Photolysis of Imazamox, Imazapic, and Imazaquin in Solutions with Natural Organic Matter. NOM is found in all river waters, commonly at concentrations between 1 and 10 mg/L.[34] Like other NOM, the Suwannee River NOM should be negatively charged at pH values of 6−9 due to carboxylic acids.[35,36] As observed in Table 4, as NOM is added into buffered solution (pH 7) with each of the imidazolinone herbicides, the photolysis reaction rate constants decrease. Two possible reasons for the decrease in reaction rate constants were considered: adsorption of the herbicides to the NOM and light screening of the NOM.

Adsorption of imidazolinones to soils and humic acids has been studied by other authors.[33,37−43] The acid−base characteristics of both the soils and the herbicides make the pH of the system important. Gennari et al. concluded that adsorption of imidazolinone herbicides to soils with high pH values (approximately >6) and low organic carbon content was weak.[33] Leone et al.'s series of papers show that mineral content in soils will play a large role in the ability of imidazolinone herbicides to adsorb.[40−42] In our experiments, the pH values were kept above 7 (where both the NOM and herbicides should be anionic, reducing any adsorption) and no inorganic compounds were present in solution or the NOM. Adsorption should play a minor role in our systems. Our experimental data support this conclusion. First, HPLC peak areas of imazamox, imazapic, and imazaquin were carefully analyzed in solutions with and without NOM. There was no sign of a decrease in peak area as NOM was added into solution, suggesting that the imidazolinone herbicides remain in solution. Second, UV/vis spectra were collected for solutions of herbicide, herbicide with NOM, and NOM solutions (see the Supporting Information). Comparisons of solutions containing imazamox, imazaquin, or imazapic with or without NOM (Supporting Information, Figure S6b−d) show that at all wavelengths, the solution containing only the herbicide had the lowest absorbance, whereas the absorbance of the solutions containing NOM and imidazolinones increased with increasing NOM concentrations. These UV/vis spectra further demonstrate that adsorption is not occurring in solution: the

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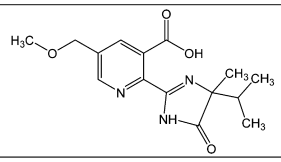
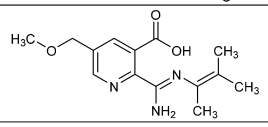
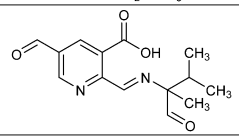
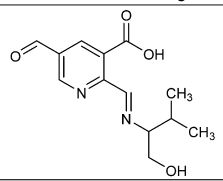
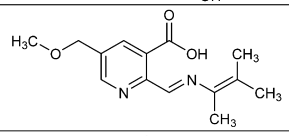
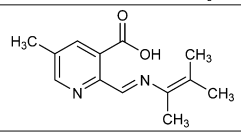
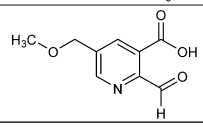
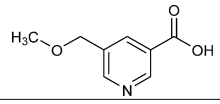
Table 5. Data from the LC-MS Mass Spectrum for Each Photoproduct of Photolysis after Irradiation of Imazamox (4.9×10^{-5} M) Samples at 310 nm for 0, 16, 30, and 60 min[a]

Photoproduct	Proposed Photoproduct Structure	Measured Mass $ESI^+ [M+H]^+$ m/z	Calculated Mass	Error (ppm)	DBE	Formula
Imazamox		306.145	306.1448	+0.7	8.00	$C_{15}H_{19}N_3O_4$
A		278.1502	278.1499	+1.02	7.00	$C_{14}H_{19}N_3O_3$
B		277.1188	277.1183	+1.87	8.00	$C_{14}H_{16}N_2O_4$
C		265.1188	265.1183	+1.96	7.00	$C_{13}H_{16}N_2O_4$
D		263.1393	263.139	+1.07	7.00	$C_{14}H_{18}N_2O_3$
E		233.129	233.1285	+2.35	7.00	$C_{13}H_{16}N_2O_2$
F		196.0606	196.0604	+0.85	6.00	$C_9H_9NO_4$
H		168.0657	168.0655	+1.08	5.00	$C_8H_9NO_3$

[a]Imazamox solutions were made in pH 7 phosphate buffers.

absorbances of the NOM/imidazolinone solutions are roughly equal to the sum of the NOM and imidazolinone solutions alone, suggesting that the two species have not changed their photochemical properties upon mixing.

The UV/vis spectra support the idea of light screening as the reason for reduction in rate constants with increasing NOM in solution. When imazamox, imazapic, or imazaquin is in solution with NOM, the NOM reduces the light reaching the herbicide. This light-screening effect has been observed for another imidazolinone herbicide, imazethapyr, when Suwanee River NOM was added to solution.[6] In the imazethapyr paper, a model was presented to account for light screening. Using this model, the photodegradation rate constants obtained in the presence of NOM can be corrected for light screening by eq 8

$$k_{corr} \approx k_{obs}^{NOM}/S(\lambda) \quad (8)$$

where k_{obs}^{NOM} is the experimental degradation rate constant for the imidazolinone in the presence of NOM and k_{corr} is the photodegradation rate constant corrected for light screening. Table 4 provides the experimental photodegradation rate constants of imazamox, imazapic, and imazaquin degradation in buffer and three NOM solutions, the screening factors for the given NOM solution and appropriate wavelength, and the photodegradation rate constants of imazamox, imazapic, and imazaquin in the three NOM solutions corrected for light screening. The screening factors for these systems ranged from 0.77 to 1.0. A value of 1.0 means there was no difference in absorbance between the imidazolinone only solution and the imidazolinone−NOM solution. The NOM had the largest effect on the imazapic rate constants, but corrections for light screening cause the photodegradation rate constants in the presence of NOM to match, within experimental error bars, the photodegradation rate constants in buffered solution for all experiments (Table 4). Overall, this analysis shows that the decrease in observed rate constants can be explained by light screening, as was shown with imazethapyr.[6]

Photoproduct Analysis for Imazamox, Imazapic, and Imazaquin. Photoproducts of imazamox, imazapic, and imazaquin were determined from irradiated samples of each

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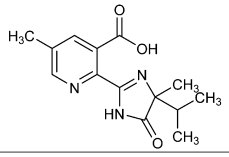
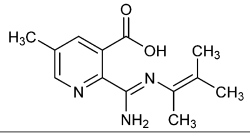
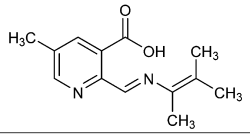
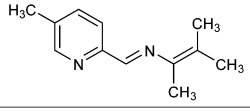
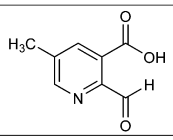
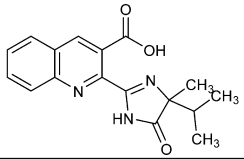
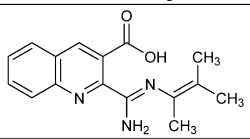
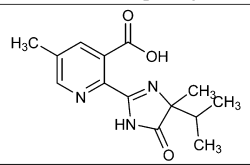
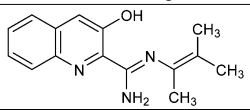
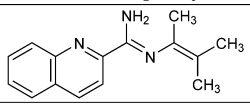
Table 6. Analysis Data from the LC-MS Mass Spectrum for Each Photoproduct of Photolysis after Irradiation of Imazapic (5.4×10^{-5} M) Samples at 310 nm for 0, 16, 30, and 60 min[a]

Photoproduct	Proposed Photoproduct Structures	Measured Mass $ESI^+ [M+H]^+$ m/z	Calculated Mass	Error (ppm)	DBE	Formula
Imazapic		276.1345	276.1343	+0.7	8.00	$C_{14}H_{17}N_3O_3$
A		248.1399	248.1394	+2.21	7.00	$C_{13}H_{17}N_3O_2$
B		233.1288	233.1285	+1.49	7.00	$C_{13}H_{16}N_2O_2$
C		189.139	189.1386	+1.99	6.00	$C_{12}H_{16}N_2$
D		166.0501	166.0499	+1.4	6.00	$C_8H_7NO_3$

[a]Imazapic solutions were made in pH 7 phosphate buffer.

Table 7. Analysis Data from the LC-MS Mass Spectrum for Each Photoproduct of Photolysis after Irradiation of Imazaquin (4.8×10^{-5} M) Samples at 310 nm for 0, 16, 30, and 60 min[a]

Photoproduct	Proposed Photoproduct Structures	Measured Mass $ESI^+ [M+H]^+$ m/z	Calculated Mass	Error (ppm)	DBE	Formula
Imazaquin		312.1343	312.1343	0	11.00	$C_{17}H_{17}N_3O_3$
A		284.1399	284.1394	+1.93	10.00	$C_{16}H_{17}N_3O_2$
B		276.1345	276.1342	+0.84	8.00	$C_{14}H_{17}N_3O_3$
C		256.1445	256.1444	+0.24	9.00	$C_{15}H_{17}N_3O$
D		240.1499	240.1495	+1.57	9.00	$C_{15}H_{17}N_3$

[a]Imazaquin solutions were made in pH 7 phosphate buffer.

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compound. Proposed product structures are presented in Tables 5−7. Detailed discussion of the proposed products for each compound is given below, but it is important to note that there are similar trends when comparing the different compounds. For example, proposed photoproducts A for imazamox, imazapic, and imazaquin are homologues. This is also observed for proposed photoproducts G for imazamox and D for imazapic. As seen in Table 3, imazaquin has a slower reaction rate; thus, samples were not degraded enough to observe this more oxidized homologue.

Proposed imazamox photoproducts along with measured mass, calculated mass, error, double-bond equivalency, and formula are summarized in Table 5. Proposed structures for photoproducts A, D, and G were determined in analysis along with confirming results found by Quivet et al. and Harir et al.[18,21] In addition, the formulas for photoproducts E and H were identified and structures were proposed in comparison with Harir et al.'s findings.[21] Photoproducts B, C, and F are products unique to this project. Photoproduct A has the same calculated mass as photoproduct I_5 in Harir et al., but the proposed structure in Table 5 differs from Harir et al.'s proposed structure in that their carbonyl carbon was lost from the carboxylic acid group, leaving the imidazole ring closed.[21] The structure for photoproduct A in this project proposes that the carbonyl group is lost from the imidazole ring, which opens the imidazole ring. Investigation into this discrepancy was analyzed using Gaussian 03 with Web−MO interface. From the computational results, it was concluded the open structure was kinetically favored with an activation energy of 108 kJ mol^{-1} compared to the closed structure with an activation energy of 277 kJ mol^{-1}. In contrast, the closed structure was favored thermodynamically with a reaction free energy change of 10.7 $kJmol^{-1}$ compared to the open structure's change of 75.9. Due to the high energy and intensity of light used in this photochemical system, the kinetic photoproduct should be favored, and the open structure of photoproduct A is proposed here on the basis of computational calculations. A similar argument can be made for all imidazolinone photoproducts as all of the compounds lost a carbonyl carbon group to form the first photoproduct.

Proposed imazapic photoproducts along with measured mass, calculated mass, error, double-bond equivalency, and formula are summarized in Table 6. Photoproducts A, B, and D all had similar theoretical masses compared to Harir et al.'s work[2] Photoproduct C is unique to this project. As with imazamox, the proposed structure for photoproduct A includes an open imidazole ring. Proposed structures for photoproducts B and D match those given by Harir et al.[2] It was observed that photoproducts A and B decreased in area as the time of irradiation increased. Alternatively, photoproducts C and D increased in area as the time of irradiation increased and were first observed at later irradiation times, suggesting that photoproducts C and D are forming from photoproducts A and B as seen in previous studies.[2,6]

Imazaquin's proposed photoproducts and results are summarized in Table 7. All photoproducts were unique to this compound when compared to photoproducts proposed by Barkani et al.[23] Imazaquin has a slower reaction rate than imazamox and imazapic that would result in the absence of lower mass, more oxidized photoproducts if not irradiated for long periods of time. The photoproducts identified by Barkani et al. were lower than m/z 220 units and were formed after being irradiated for 390 min at wavelengths of ≥290 nm. In this study, the photoproduct with the lowest observed measured mass was at m/z 232 units, but the samples in this study were irradiated for only 60 min at 310 nm. Perhaps if irradiated longer, the samples here would have further photodegraded, reaching photoproducts with lower measured masses. As with imazamox and imazapic, the proposed structure for photoproduct A includes an open imidazole ring. Interestingly, imazapic is a proposed photoproduct formed from irradiation of imazaquin (photoproduct B), something not previously observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.5b04663.

Chromatogram showing the resolution between imazamethabenz-methyl isomers; [OH−] dependence of the observed first-order hydrolysis rate constant, k_{app}; data on the pH dependence of the photolysis of imazmox, imazapic, and imazaquin; UV/vis spectra for solutions of herbicide, herbicide with NOM, and NOM solutions for imazamox, imazapic, and imazaquin (PDF)

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Notes

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