



KINETICS OF PHOTOCHEMICAL DEGRADATION OF IMAZAPYR IN AQUEOUS SOLUTIONS

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ABSTRACT

Kinetic parameters of imazapyr photodegradation in aqueous solutions are presented at two pH values and different concentrations. To study the effect of UV and sunlight irradiation, reactions were carried out by using a pyrex reactor equipped with UV high pressure mercury arc and a solar simulator (Heraeus Suntest CPS+). The depletion of imazapyr concentration always followed first order kinetic. The half-lives were 19.0 and 24.7 minutes at pH 7.0 and 4.0, respectively. The influence of organic matter on the photolytic process was studied irradiating a solution of imazapyr with suspended humic acids (1:1 w:w).

Key words: photodegradation, herbicide, imazapyr, humic acid, kinetic

Introduction

Imazapyr [2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2yl)nicotinic acid], Figure 1, is an imidazolinone herbicide which inhibits acetohydroxyacid synthase. It is a broad-spectrum herbicide, highly soluble in water (1), used to control annual and perennial grass and broad-leaved weeds, applied either pre or post-emergence (2-4) in non cropped areas such as roadsides, along railroads, pipelines and industrial areas (5). It has been tested for weed control in cereal crops and sugar beet in Morocco. The benefits yielded by imazapyr lead to its more intensive application in

the environment, nevertheless, little information is available about its persistence and degradation behaviour.

Imazapyr photoreactivity has been already tested under simulated sunlight conditions using a borosilicate-filtered xenon arc (6). Half-lives calculated from first-order model ranged from 1.9 to 2.3 days in distilled water. At buffered pH 5, half-life was 2.7 days; meanwhile at pH 9 resulted 1.3 days (1). Photolysis essentially leads to four major compounds, with a substantial production of carbon dioxide (6). Photodegradation of imidazolinone herbicides occurs also in the soil, where the half-life is observed to be higher than in laboratory experiments, and is influenced by soil chemical properties and water potential (7, 8).

Humic acids have been found to act as photosensitizers when irradiated at a wavelength $>290\text{nm}$ (9, 10).

Exposition to UV light or simulated sunlight is a very useful method for testing the susceptibility to photolysis of pesticides.

In this work, UV and sunlight photodegradations of imazapyr were studied in order to obtain new information on the herbicide behaviour at different pH values and concentrations in water and in the presence of humic substances.

In fact, even if the irradiating energies are different, comparison between kinetics of UV and sunlight photolyses is very important in understanding the reaction pathway.

Materials and Methods

Imazapyr was purchased from Dr. Ehrenstorfer, Germany, and solutions (0.04 and 0.11 mM) were prepared in ultrapure bidistilled water (pH=6.4).

Solution at pH 4 was obtained by adjusting pH with H_3PO_4 ; pH 7 was reached by using $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ buffer (1.15:1; w:w; ionic strength = 0.05 M). Photodegradation was performed employing a Pyrex reactor (250 mL) equipped with UV high pressure mercury arc (Philips HPK 125W, $\lambda \geq 290\text{ nm}$ glass filtered).

The effect of the presence of humic acids in aqueous solutions on the photolysis of imazapyr was also investigated exposing a 1:1 (HA:herbicide, w:w) suspension to UV arc.

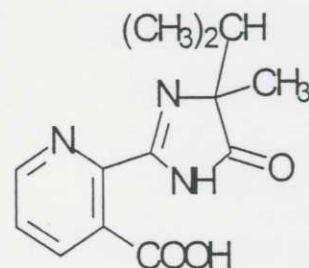


Fig. 1 Chemical structure of imazapyr

Humic acids purchased from Aldrich Co were used without further purification. Characterization of HA was carried out by chemical and spectroscopic methods (Tables 1 and 2) (11,12).

Table 1. Chemical characteristics of HA

Humic Acids	N %	C %	H %	O %	Ash %	H ^a	COOH	OH
							cmol kg ⁻¹ (meq 100 g ⁻¹)	
<i>Aldrich</i>	0.5	48.4	4.7	46.4	7.4	8.9	3.2	2.9

Table 2. IR spectroscopic characteristics of HA

Wavenumbers (cm ⁻¹)	Assignments	Band Intensity
3600-3380	O-H or N-H str.	B, S
2980-2900	Aliph. C-H str. in CH ₂ and CH ₃	N, S
2880-2815	Str. C-H alif., str. C-H aldehydes	N, W
1730-1700	Vibr. str. C=O (aldehydes, chetones, carboxyl. acids)	N, W
1620-1590	C=C str.alif. and arom.	B, S
1420-1320	Deform. of aliph. C-H or OH, str. of C-O in phenol	B, M
1300-1250	C-O str. ethers, carboxylic acids, esters	B, W
1050-1020	C-O str. in various groups	N, W
1000-650	Bend =C-H groups, vibr.of COOH	B* M

*S, Strong; M, Medium; W, Weak; B, Broad; N, Narrow; P, Shoulder; * several absorptions.*

Irradiation under simulated sunlight (Heraeus Suntest CPS+; xenon arc; 290-800 nm; 765 W m⁻²) was carried out adding TiO₂ (1 mg kg⁻¹) to the samples with the aim of accelerating the photodegradation process. In fact, preliminary investigation showed a very limited degradation of the active ingredient after 2 days. Control solutions were kept in the dark to verify the possibility of hydrolysis reactions. Temperature was fixed at 25 °C.

Actinometric measurements, performed by using uranyl oxalate photoreaction, indicated that efficiencies of UV and xenon arcs did not diminish during the experimental time (13).

The herbicide degradation and by-products yielded were monitored at different exposition times by HPLC (HP 1090L) equipped with diode array detector, wavelength 230 nm, 5 µl loop, column Dionex Omnipac PCX-500 20 cm x 3.2 cm i.d.. The mobile phase was a mixture of water (pH=3; H₃PO₄) and acetonitrile (75:25; v:v); the flow rate was 1 mL min⁻¹.

Detection limit of the analytical method was 0.3 mg L^{-1} and linearity of calibration curve was observed up to 40 mg L^{-1} ($r^2=0.9997$).

Kinetic parameters were calculated using first and second order equation and the best fit was checked by regression analysis.

Statistical data were calculated by Microsoft Excel 5.0.

Results and discussion

a) UV mercury arc

Fig. 2 shows that the disappearance of imazapyr in distilled water does not depend on concentration under UV irradiation.

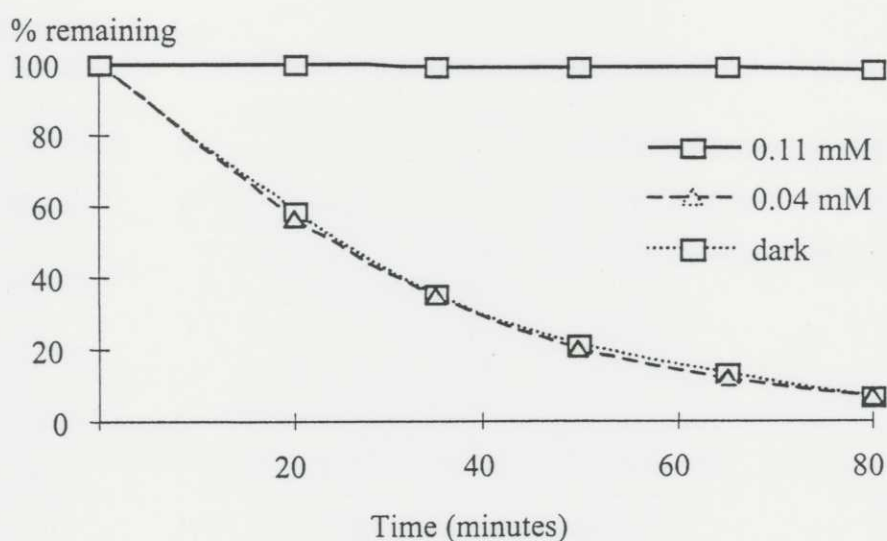


Figure 2. Disappearance of imazapyr in water at two concentrations

The concentration of imazapyr in the dark was not modified during the experimental time. In agreement with literature data (6), no hydrolysis reaction was observed at the investigated temperature.

In Figure 3 the disappearance of the herbicide in buffered solutions is reported. Half-lives of the herbicide due to photoreaction were 19.0 and 24.7 minutes at pH 7 and pH 4, respectively. The detection limit of the used analytical method was reached after 97 minutes at pH 4 and 72 minutes at pH 7.

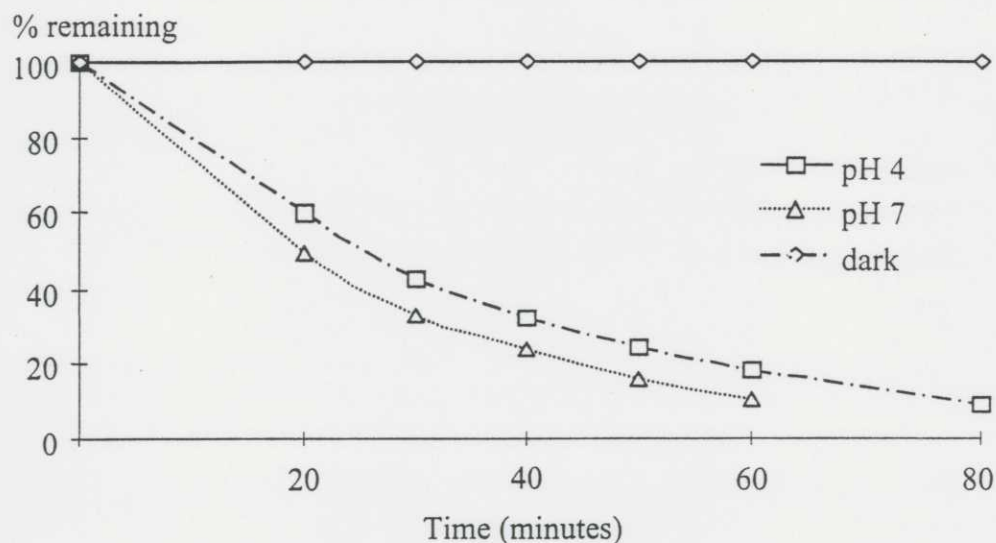


Figure 3. Comparison of UV photolysis of imazapyr 0.11 mM at two pH values

Table 3. Kinetic parameters of imazapyr (0.11 mM) photoreactions at different pH values.

n	K(min ⁻¹)	pH 4			pH 7			nat. pH		
		t _{0.5} (min)	r ²	k(min ⁻¹)	t _{0.5} (min)	r ²	k(min ⁻¹)	t _{0.5} (min)	r ²	
1	0.0281	24.67	0.993	0.0365	18.99	0.994	0.0318	21.80	0.991	
2	0.5709	15.72	0.883	0.8237	11.59	0.863	0.5812	15.01	0.892	

n = reaction order; *k* = kinetic coefficient; *t*_{0.5} = half life; *r*² = regression coefficient

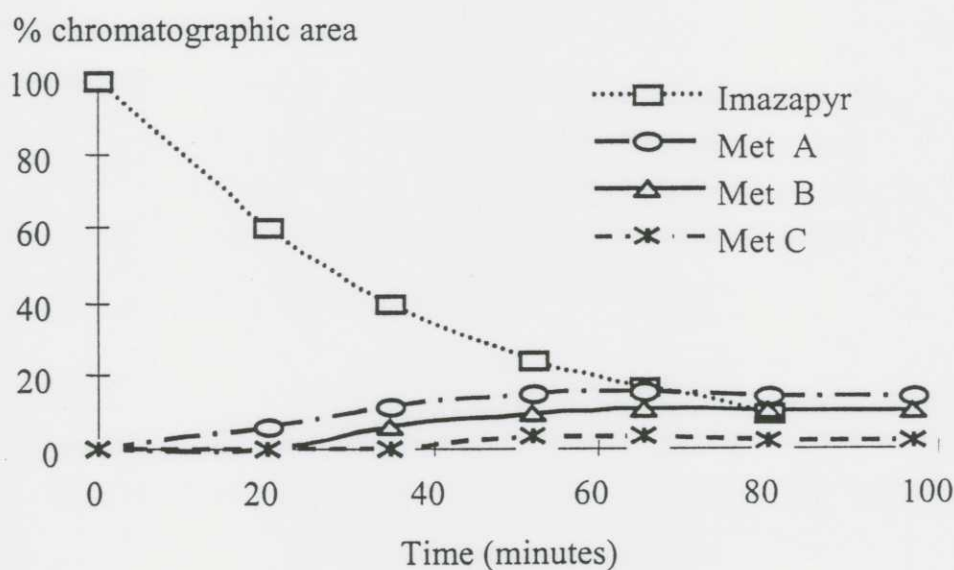


Figure 4. Depletion of imazapyr 0.11 mM at pH 4 and appearance of metabolites

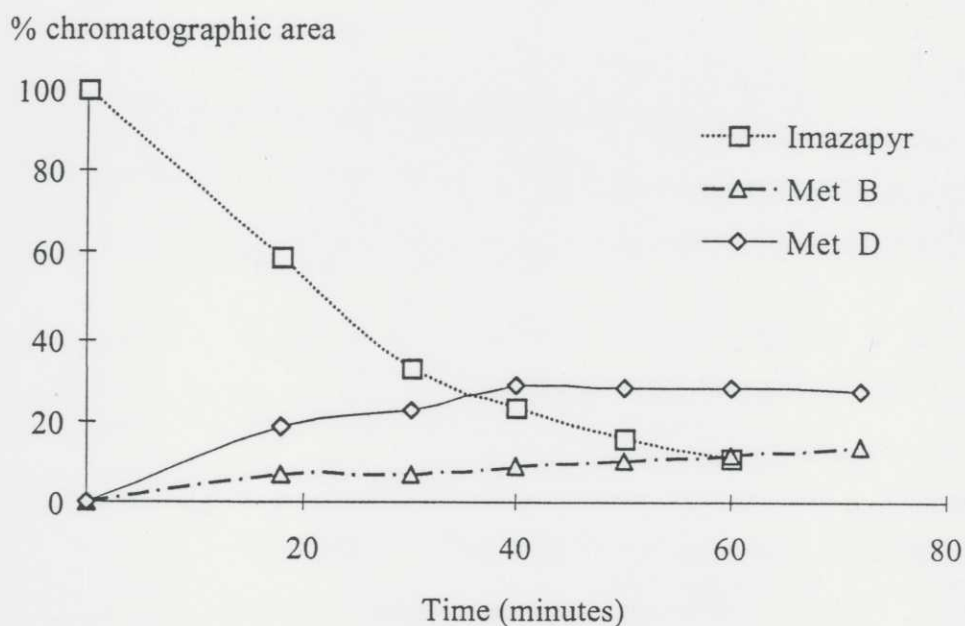


Figure 5. Depletion of imazapyr 0.11 mM at pH 7 and appearance of metabolites

In Table 3 are reported the kinetic parameters of imazapyr photoreaction at different pH values for the concentration 0.11 mM. The values of the regression coefficients indicate that the best fit is reached considering a first order reaction and the half-lives are affected by pH values of the solution. Four main metabolites, labelled A, B, C, D, with different retention times and UV spectra were obtained (Figures 4 and 5). These indications, together with literature data (1), allow their identification as quinolinic acid (A); quinolinimide (B); 7-hydroxy-furo[3,4-b]pyridine-5(7H)-one (C); furo[3,4-b]pyridine-5(7H)-one (D). At pH 4 chromatographic response of metabolite D was below the detection limit, while at pH 7 the same happens for photoproducts A and C. Retention times and capacity factors of the four metabolites are reported in Table 4.

Table 4 Chromatographic parameters of imazapyr and metabolites

	UV pH 4		UV pH 7		UV HA		Sunlight	
	t_r (min)	k'	t_r (min)	k'	t_r (min)	k'	t_r (min)	k'
Imazapyr	13.11	4.7	12.88	4.60	13.85	4.77	13.20	5.00
Met A	3.04	0.32			3.10	0.29	2.94	0.34
Met B	4.55	0.98	4.62	1.01	4.70	0.96	4.68	1.13
Met C	3.64	0.58						
Met D			22.75	8.89				

t_r = retention time; k' (capacity factor) = $(t_r - t_0)/t_0$

The half-life of imazapyr in the humic acid suspension was higher (42.3 minutes) than in pure solution (21.8 minutes). During the photochemical reaction in the HA suspension the presence of metabolites A and B was observed. Metabolite B appeared after 100 minutes of irradiation, while in the absence of HA it was found at 20 minutes. The protective effect of HA on the imazapyr degradation could be explained as due to inclusion and/or adsorption of the herbicide molecules in the humic matrix; moreover, the organic matter could behave as a quencher (14-15) or could cause the scattering of light. Table 5 reports kinetic parameters of photochemical reaction of imazapyr in HA suspension calculated for the first and second order reactions. The best fit was found at first order.

Table 5. Kinetic parameters of imazapyr in HA suspension.

n	k (min ⁻¹)	t _{0.5} (min)	r ²
1	0.0164	42.26	0.997
2	0.3553	24.64	0.883

n = reaction order; *k* = kinetic coefficient;
*t*_{0.5} = half life; *r*² = regression coefficient

Table 6. Kinetic parameters of imazapyr under Suntest irradiation.

n	k (min ⁻¹)	t _{0.5} (min)	r ²
1	0.0025	277.26	0.959
2	0.0567	182.97	0.766

n = reaction order; *k* = kinetic coefficient;
*t*_{0.5} = half life; *r*² = regression coefficient

b) Xenon arc

Imazapyr photodegradation induced by simulated sunlight in the presence of TiO₂ reached the detection limit in about 10 h. In the dark the catalyst did not produce any degradation effect on the imazapyr molecule.

Degradation of herbicide in water (0.11 mM + 1 mg kg⁻¹ TiO₂) showed the presence of metabolites A and B, but photoproducts C and D were below the detection limit.

The best fit calculation of kinetic data leads to a first order reaction (Table 6) but the presence of TiO₂ could have influenced the pathway of photolysis. Further studies are in progress to explain the role of the catalyst in the photolysis mechanism.

Conclusions

The concentration decline of imazapyr in UV irradiated solutions followed a first order kinetic and photolysis rate increased with pH value, as reported in literature. Initial studies on sunlight induced degradation show that the semiconductor TiO₂ plays a fundamental role on the photolysis rate. Humic acids induced a decrease of the degradation rate with respect to pure water solution. This

evidence is probably due to a sort of protective effect of the humic substances on the pesticide molecules and/or a competitive effect attributable to the photons capture by organic molecules.

Acknowledgements

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