



Photochemical Degradation of Imazethapyr Herbicide in Aqueous Media

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The photodegradation process of imazethapyr (IMZT) has been investigated under simulated sunlight using HPK lamp in aqueous media. In order to examine the effect of pH, we irradiated the solution at pH 2.7, 3.5, 4, 5.7 and 9. The photodegradation of imazethapyr appears to be more effective when $\text{pH} > \text{pK}_a$ and in the absence of oxygen. The major photodegradation products formed mainly by a photohydrolyze process and Norrish II reaction.

Key Words: Herbicide, Imazethapyr, Photochemical degradation.

INTRODUCTION

It is now well admitted that when pesticides are dispersed in the environment, different mechanism of degradation can occur including biodegradation, hydrolysis and photodegradation. Recently it has been shown that according to the experimental conditions, direct photolysis could play an important role in the attenuation in the environment of these compounds. In addition, during the degradation mechanism, numerous intermediates are generated which could be more toxic than the parent compounds so that their careful identification is strongly required¹.

Imidazolinones are a new class of low rate, reduced-environmental risk herbicides for the protection of wide variety of leguminous crops including soybeans². Their effect is based on inhibition of the enzyme acetohydroxyacid synthase, the feedback enzyme involved in the biosynthesis of the branched-chain amino-acids: valine, leucine and isoleucine³. Injury symptoms are slow to develop (one to two weeks) and include stunting or slowing of plant growth and a slow plant death.

This study was designed to develop the evolution of imazethapyr, an herbicide belonging to the imidazolinone family, in aqueous solution. imazethapyr is highly soluble in water (11.3 g/L), however concentration of imazethapyr would be found in water and groundwater will exceed the CE limit and will be a potential pollutant of water⁴.

We report in this work the kinetic data of imazethapyr photodegradation in aqueous solution at different pH, wavelengths and oxygen concentrations.

It has been found that the main mechanisms of the degradation were a hydrolysis of the imidazole ring, a condensation *via* the carboxylic acid and a breakdown of the C-C bond binding the quinoline moiety. The information provided by this study could be of aid in the understanding of the environment behaviour of this herbicide.

EXPERIMENTAL

Imazethapyr (acid 2-[4,5-dihydro-4-methyl-4-(1-methyl-ethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic), purity > 99 % was purchased from Aldrich (Fig. 1). It was used without further purification.

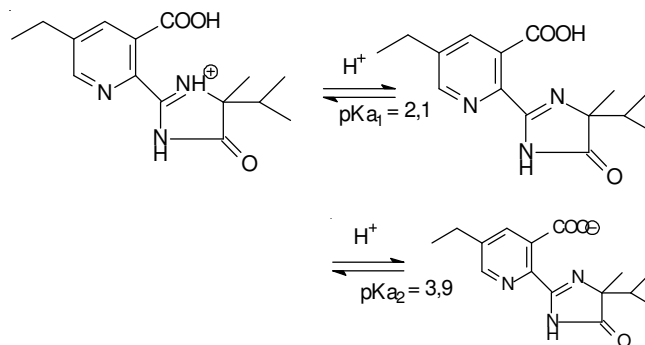


Fig. 1. Chemical structure of imazethapyr⁵

Phosphates buffers (KH_2PO_4 and K_2HPO_4) were purchased from Carbo Erba. The solutions were buffered at $\text{pH} = 7$. pH was adjusted by addition of NaOH or H_3PO_4 .

The solvents used for HPLC analysis were acetonitrile, HPLC grade from SDS and formic acid purchased from Prolabo.

The irradiated solutions (50 ppm) were prepared from a concentrated imazethapyr solution (200 ppm) stored at 4 °C. The deoxygenation and saturation of the solutions were accomplished by bubbling argon for 0.5 h at room temperature before irradiation and then bubbling was maintained during all the irradiation.

All the solutions were prepared with ultra pure water obtained with A MILLI-Q DEVICE (Millipore) and its purity was controlled by resistivity. The pH measurements were carried out with a Meterlab pH meter.

Irradiation experiments: Two kinds of photoreactors were used. In the first one, the irradiation experiments were carried out using a high pressure mercury UV lamp (Phillips HPK 125 W) equipped with 50 mL cylindrical reactor made of Pyrex in order to obtain simulates sunlight (wavelengths > 290 nm). Experiments were carried out at 20 °C under different atmospheres. In the second photoreactor, the irradiation experiments were carried out using a low pressure mercury lamp (Phillips 6W) equipped with a quartz cell of 1 cm path length.

Quantum yield quantum efficiency: The quantum yield is defined as the ratio of the number of transformed molecules and the number of absorbed photons during the same irradiation time. This measurement reflects the efficiency of the photochemical reaction. The photon flow was evaluated by means of classical ferrioxalate actinometry.

The polychromatic quantum efficiency (η) values were calculated using a software, "Photon" well described earlier⁶.

Formula I

$$\phi = \frac{N_d}{P_{\text{abs}}} \quad (\text{Monochromatic light})$$

Formula II

$$\eta = \frac{N_d}{\Sigma P_{\text{abs}}} \quad (\text{Polychromatic light})$$

Analytical procedures: To follow the disappearance of imazethapyr HPLC analyses were conducted using an instrument Varian 9010, equipped with a mono-channel UV-visible detector and a Shimadzu LC10AT apparatus equipped with a photodiode array detector. The column used was a Hypersil ODS C₁₈ column (5 μm , 150 mm \times 4 mm) and a pre-column; the flow rate of isocratic elution was 1 mL min⁻¹ and the injection volume was 20 μL . The isocratic mobile phase was a mix of acetonitrile (A) (25 %) and buffered water at pH 3, using formic acid, as co-solvent (B). Whereas to follow the appearance of the photoproducts a gradient of (A) and (B) was used: from 10 % of (A) to 75 % during 15 min.

UV-Visible absorption spectra were recorded with a double beam UVIKON 930 Spectrophotometer (Kontron Instruments).

HPLC-MS studies were carried out with Hewlet-Packard HP 1100 Series LC-MSD. It is equipped with an Uptispherc 3HDO, column (3 μm , 100 mm \times 2 mm) and thermostat 40 °C. It was used with the same operating conditions than the HPLC-UV analysis. The injection volume was 50 μL . The MS detection

was performed using an electrospray ionization (ESI) in positive and negative modes. Ionization conditions of ESI analysis were as follows: capillary potential 300 V; N₂ flow 13 L min⁻¹, pressure 55 psig.

RESULTS AND DISCUSSION

Photophysical properties of imazethapyr: Fig. 2 presents the absorption spectra of imazethapyr in aqueous solution at different pH.

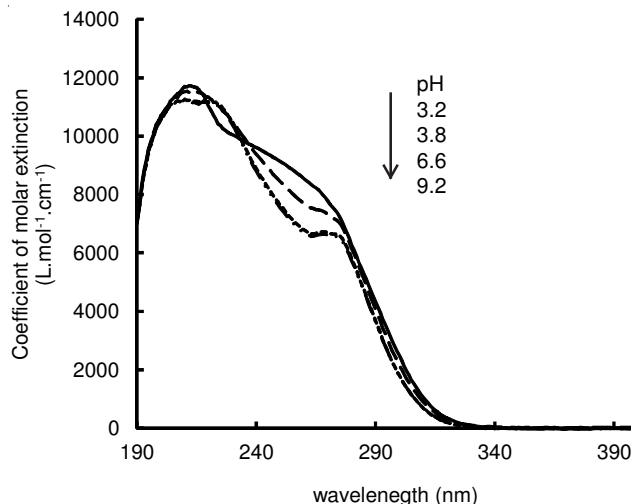


Fig. 2. Absorption spectra of imazethapyr in aqueous solutions at different pH

The curves present a measurable absorption with a tail up to 320 nm. According to the European Community directive (94/37/CE), the photo transformation of pesticides must be taken into account if the molar extinction coefficient is superior to 10 L mol⁻¹ cm⁻¹ for $\lambda > 290$ nm. So, the photodegradation of imazethapyr must be studied.

The observation of the UV-VIS absorption spectra of the imazethapyr show two maxima which are less marked. Their form changes according to the pH and broadly the molar extinction coefficients of imazethapyr are weaker. The first absorption band is particularly large at pH 9 and stretch from 200 and 240 nm ($\epsilon_{220 \text{ nm}} = 11\,500 \text{ L mol}^{-1} \text{ cm}^{-1}$) and the second one around 280 nm is larger at pH 3.2 and stretch from 230 and 290 nm ($\epsilon_{280 \text{ nm}} = 8400 \text{ L mol}^{-1} \text{ cm}^{-1}$).

Kinetic studies

Influence of the pH on the kinetic of photodegradation and on the quantum efficiency (polychromatic): The effect of pH on the photodegradation kinetics of imazethapyr has been evaluated under simulated sunlight irradiation ($\lambda \geq 290$ nm). The disappearance of imazethapyr follows an apparent first-order kinetic whatever the pH values studied.

The influence of pH on the kinetic constants of imazethapyr degradation rate constant was illustrated by Fig. 3.

The rate constant of imazethapyr increase with the increase of pH, ranging for from 13×10^{-4} at pH 2.7- 43×10^{-4} at pH 7. If we bring closer these results to the precedent: the pesticide present a pK_{a2} about 3.9 so we can say that its kinetic of photodegradation is faster for the anionic form than the molecular form. The quantum efficiencies calculated are presented

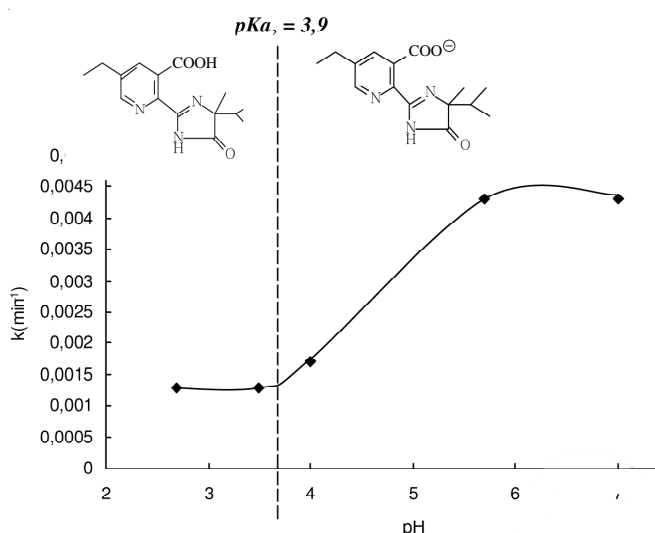


Fig. 3. Evolution of the rate constant (k) of the photodegradation of imazethapyr as a function of pH

in Table-1 and the values obtained show first that the quantum efficiency is pH dependent and second that the anionic form is more highly reactive.

pH	2.7	3.5	4.0	5.7	9.0
$\eta \cdot 10^3$	0.57	0.79	1.82	1.80	2.55

Influence of the wavelength on the quantum yield (monochromatic wavelength): The wavelength effect on the photochemical behaviour of imazethapyr was studied with solutions ($C = 50$ ppm) irradiated at pH = 3.5 in quartz reactor using a monochromator. Table-2 put in evidence that quantum yield of imazethapyr changed with the wavelength (at $\lambda = 254$ nm it is 5 once more to others wavelengths).

λ (nm)	254	270	290
$\Phi_{\text{IMZT}} \times 10^3$	27	5	6

The influence of wavelength on quantum yield and a phototransformation of the imazethapyr was more effective at 254 nm and can suggest an influence of a keto-enolic equilibrium. Erre and Coll⁷. has yet suggest a tautomerization of the imazapyr (pesticide of the imidazolinone family) to explain the fact that a basic nitrogen available for the coordination with copper complexes. Faure⁸ observed that the ketonic form absorbs shorter wavelengths than the enolic form. The excited forms obtained with the short wavelengths, would come mainly from the ketonic form.

Influence of the concentration on the quantum yield: In order to examine the effect of the concentration, aqueous solutions of imazethapyr (12, 25, 50 ppm) were exposed to the simulated sunlight. The calculated quantum yields at different concentrations of imazethapyr shows a variation when concentration increases from 12-50 ppm. So the reaction can be supposed bimolecular for the imazethapyr (Table-3).

[IMZT] (ppm)	12	25	50
Φ_{IMZT}	0.019	0.021	0.027

Influence of oxygen concentration: To evaluate the role played by the oxygen on the photodegradation, we have irradiated imazethapyr under different atmospheric conditions (Table-4).

Conditions	[O ₂] (mol L ⁻¹)	$k \times 10^3$ (min ⁻¹)	
		IMZT	
Deoxygenated solution	$< 10^{-5}$	2.7	
Aerated solution	2.6×10^{-4}	2.5	
Oxygen saturated solution	1.3×10^{-3}	2.4	

The rate constant of photolysis is higher in the deoxygenated solution than in oxygen saturated solution. On the other hand, similar values are obtained for the disappearance of imazethapyr in deoxygenating solution and oxygen naturally present in the aerated solution.

Identification of photoproducts: Analysis and identification of photoproducts of the imazethapyr was determined.

To identify the imazethapyr photoproducts, we used a chromatographic system HEWLET-PACKARD HP1100 series LC- MSD whose detector of masses is a quadruple of range from 50-1500 mA. Ionization was carried out by electrospray (ESI) in modes negative and positive. The typical fragments of photoproducts are summarised in Table-5.

Composé	Imazethapyr	Photoproduct 1	Photoproduct 2
Structure			
t_r (min)	14	6,8	7,3
[M + H ⁺]	290	177	195

There are two major photoproducts ($tr_1 = 6, 8$ min and $tr_2 = 7, 3$ min). According to the mass spectra we could affect the chemical structures illustrated in Table-5. Another photoproduct was detected at $tr = 12, 7$ min ($M = 441, 2$) is almost twice the mass of the imazethapyr. This photoproduct could be formed by a process of dimerization.

Proposed reaction pathway: The coupling of HPLC-MS enables us to propose a photochemical way of evolution of the imazethapyr in aqueous solution. The formation of the photoproduct 2 could be explained by a mechanism of photohydrolyse which involves an opening of imidazole ring, following-up of a standard reaction of Norrish II. Hydrogen in position γ is in the same plane than the function carbonyl and its displacement can be affected to this type of reaction. The photoproduct 1 comes then from the transformation of the photoproduct 2 by the loss of a molecule: dehydration (Fig. 4).

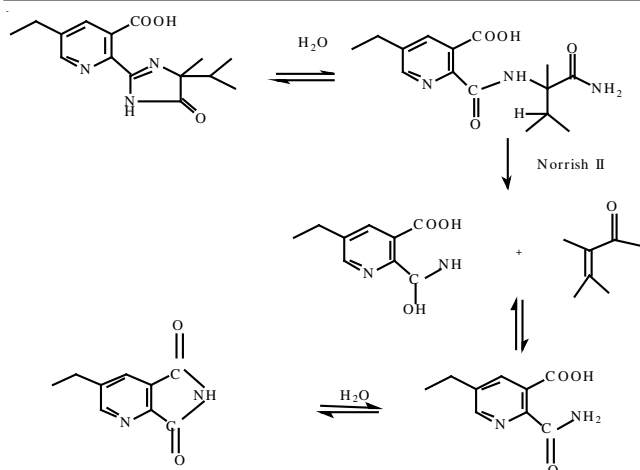


Fig. 4. Pathway of imazethapyr photodegradation

Conclusion

The photodegradation of imazethapyr was investigated using simulated sunlight irradiation at different pH values, different wavelengths and different oxygen concentrations. This work shows the influence of the pH on the photochemical

behaviour of the imazethapyr in solution. The ionic form of the carboxylic function photodegrade more quickly than the molecular form and in the absence of oxygen.

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