

# Kinetics and Mechanisms of Abiotic Degradation of Fipronil (Hydrolysis and Photolysis)

Alain Bobé,<sup>†</sup> Pierre Meallier,<sup>‡</sup> Jean-François Cooper,<sup>\*,†</sup> and Camille M. Coste<sup>§</sup>

Laboratoire de Chimie Analytique, Faculté de Pharmacie, Avenue Charles Flahault, 34060 Montpellier, France; Laboratoire d'Application de la Chimie à l'Environnement, Université Claude Bernard, Boulevard du 11 Novembre 1918, Lyon, France; and Centre de Phytopharmacie, Avenue de Villeneuve, 66000 Perpignan, France

The abiotic degradation of fipronil (compound **I**), a phenylpyrazole insecticide, was studied in aqueous solution and on the surface of two soils from Niger (Saguia and Banizoumbou) and one Mediterranean soil (Montpellier). The rate of hydrolysis of fipronil in solution was measured at different values of pH and temperature. The pH was an influencing factor: hydrolysis kinetics were pseudo-first-order, the half-life being 770 h at pH 9.0, 114 h at pH 10.0, 11 h at pH 11.0, and 2.4 h at pH 12.0. Fipronil was stable under acid (pH 5.5) and neutral conditions. The Arrhenius relation was verified over the temperature range 22–45 °C: the activation energy was 62 kJ mol<sup>-1</sup> and the calculated entropy change -32 J mol<sup>-1</sup>. Compound **II** [5-amino-3-carbamoyl-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-[(trifluoromethyl)sulfinyl]pyrazole] was the only hydrolysis product detected. The hydrolysis reaction mechanism involves nucleophilic addition of OH<sup>-</sup> to the polar nitrile bond, producing a hydroxyimine which then undergoes tautomerization into an amide. Fipronil in acidic (pH 5.5) aqueous solution exposed to light from a xenon lamp degraded with first-order kinetics ( $K_{obs} = 1.7 \text{ h}^{-1}$ ) with concomitant appearance of 5-amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethyl)pyrazole (compound **III**) and 5-amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)pyrazole-4-sulfonic acid (compound **IV**). The photolyte formation rate constants were 0.11 h<sup>-1</sup> (**III**) and 0.05 h<sup>-1</sup> (**IV**). The observed degradation process corresponded to a desulfinylation and an oxidation. The reaction mechanisms were not elucidated. The irradiation (xenon lamp) of fipronil adsorbed on three natural soils when dry led to the formation of 4-(trifluoromethyl)pyrazole (**III**). The  $K_{obs}$  values were 0.0047 h<sup>-1</sup> (Saguia), 0.0039 h<sup>-1</sup> (Banizoumbou), and 0.0032 h<sup>-1</sup> (Montpellier). The degree of photodegradation was inversely proportional to fipronil adsorption: the Freundlich adsorption coefficients were, respectively, 4.3 (Saguia), 7.3 (Banizoumbou), and 45.5 (Montpellier).

**Keywords:** Fipronil; hydrolysis; photodegradation; kinetics; soils; degradation products

## INTRODUCTION

Fipronil [5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]pyrazole; compound **I**] is a phenylpyrazole insecticide recently developed by Rhône-Poulenc Agro. Applied at low doses, it is active against a wide range of insect pests of crops, notably rice insects, thrips (citrus, cotton, mango, . . .), termites (sugar cane, corn), and click beetles (cereals, corn, sunflower, beets, . . .) (Gailliard, 1996). It has also been recommended for use in locust control (Balança and De Visscher, 1997). Its wide range of action (locust and grasshoppers, ready-to-hatch eggs, larvae, and imagos) and multiple uses (total cover or barrier treatment, possible use in preventive or curative control, in agricultural, forestry, or pastoral zones) seem to give it an advantage over growth regulators in chemical locust control (Rachadi, 1995). Fipronil has been shown to interfere with the passage of chloride ions through the  $\gamma$ -aminobutyric acid regulated chloride channel, thereby

disrupting central nervous system activity and, at sufficient doses, causing death (Cole et al., 1993).

Laboratory and field studies on different soil types (loam, silt loam, clay loam, sand, . . .) under temperate conditions (United States, Europe) have enabled Rhône-Poulenc to identify five principal metabolites: 5-amino-3-carbamoyl-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]pyrazole (compound **II**), 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)pyrazole (compound **III**), 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]pyrazole-4-sulfonic acid (compound **IV**), 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)sulfonylpyrazole, and 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)thio]pyrazole. Different degradation pathways have been proposed: hydrolysis, photolysis, oxidation, and reduction.

As part of locust control trials, we set up a study on the open field behavior of the product under Sahelian conditions (Niger, Niamey region, October 1995). The amide (**II**) and trifluoromethylpyrazole derivative (**III**) were the principal degradation products recovered from the soil (Bobé et al., 1998). In the absence of additional bibliographic data, we wished to confirm in the labora-

\* Author to whom correspondence should be addressed (fax 33 4 67 54 45 26; e mail jcooper@pharma.univ-montp1.fr).

<sup>†</sup> Laboratoire de Chimie Analytique.

<sup>‡</sup> Laboratoire d'Application de la Chimie à l'Environnement.

<sup>§</sup> Centre de Phytopharmacie.

**Table 1. Some Physical and Chemical Properties of the Three Soils**

soil	pH (H <sub>2</sub> O)	sand (%)	silt (%)	clay (%)	CEC	
					(mequiv/100 g)	organic matter (%)
Banizoumbou	5.8	79.4	18.2	2.4	0.7	0.3
Sagua	5.3	98	1.4	0.6	0.7	0.1
Montpellier	8.3	54.4	23	22.6	23.5	6.5

tory the formation of these degradation products during hydrolysis and photolysis reactions carried out in aqueous solution and/or on adsorbed material (Sahelian soils) and to attempt to propose reaction mechanisms.

The influence of various parameters was studied: pH and temperature for the hydrolysis reactions and the nature of soil for photolysis of adsorbed fipronil. A comparative study including a Mediterranean soil with different physical-chemical characteristics was carried out to complement the evaluation of soil influence.

## MATERIALS AND METHODS

**Chemicals.** Fipronil [5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)sulfinylpyrazole] (compound **I**), 5-amino-3-carbamoyl-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)sulfinylpyrazole (compound **II**), 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)pyrazole (compound **III**), and 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]pyrazole-4-sulfonic acid (compound **IV**) were supplied by Rhône-Poulenc Agro (Lyon, France) as analytical standards (purity  $\geq 99.4\%$ , except for the derivative acid sulfonic with 94.4% purity). Stock solutions were prepared at 250 and 25 mg L<sup>-1</sup> in methanol and stored at 4 °C. Working solutions were prepared by dilution in pure water or in toluol. Solvents were pesticide residue analysis grade (toluol) or HPLC grade (acetone, methanol, acetonitrile, water). Sodium hydroxide, hydrochloric acid, anhydrous sodium sulfate, and acetic acid were analysis grade. Tetrabutylammonium hydroxide, 40 wt % solution in water, was purchased from Sigma-Aldrich, France. Reversed phase octadecyl (Sep-Pak Classic, short body C<sub>18</sub>) disposable cartridges for solid-phase extraction (SPE) were obtained from Waters, France. Glass-microfiber filters GF/B were obtained from Whatman.

**Soil Characteristics.** Three uncontaminated surface soils were collected under Sahelian (0–10 cm depth) or Mediterranean (0–30 cm depth) conditions: two from the Republic of

Niger—to the south (Sagua) and the west (Banizoumbou) of Niamey—and one from the region of Montpellier in the south of France. On the basis of U.S. Soil Taxonomy, Banizoumbou and Sagua surface soils can be classified as Entisols (*troposammets*), respectively, loamy sand and sand, while Montpellier soil belongs to the Inceptisols group (*eutrochrept*). Samples were air-dried, passed through a 2 mm sieve, and stored at 4 °C to minimize changes in their microbial populations. Their physical and chemical properties, determined by the Soil Laboratory, CIRAD, Montpellier, are summarized in Table 1.

**Apparatus.** The following equipment was used in this study: classical laboratory glassware and equipment (water bath, rotary evaporator, . . .); a Beckman DU 460 UV-vis spectrophotometer; a solar simulator (Suntest), fitted with a xenon lamp (1.8 kW, 14.6 A); UV filters for adjustment of the UV spectral limit; a parabolic reflector to ensure even distribution of light in the irradiation chamber (exposed area 500 cm<sup>2</sup>); and a ventilation cooling system (21 °C). The emission spectrum (290–800 nm) was very close to that of sunlight with optimum simulation up to 460 nm. High-performance liquid chromatography was run under the following conditions: Spectra system P1000; 20  $\mu$ L injection loop; C<sub>18</sub> Hypersil column (200 mm  $\times$  4.6 mm  $\times$  5  $\mu$ m); UV detector, Shimadzu SPD6-A set at 220 nm; mobile phase, acetonitrile (ACN)/water + tetrabutylammonium hydroxide (TBAH) (5 mM) + 0.5 M HCl to adjust pH to 5.0; elution gradient, 0 min ACN/TBAH (45:55), 6 min ACN/TBAH (60:40), 20 min ACN/TBAH (60:40), 25 min ACN/TBAH (45:55); flow rate, 1 mL min<sup>-1</sup>. The retention times of fipronil and its three degradation products are given in Table 2. A Hewlett-Packard HP 5890 gas chromatograph was connected to a mass spectrometric (MS) detector HP MSD 5971A with the following conditions: electron impact mode, 70 eV; splitless injection mode (injection purge off = 0.75 min); injector temperature, 250 °C; transfer line temperature, 280 °C; column, SPB-17, 30 m, 0.25 mm i.d., 0.25  $\mu$ m film thickness; initial oven temperature, 70 °C for 1 min raised at 50 °C min<sup>-1</sup> to 240 °C for 16 min; solvent delay, 3 min; carrier gas, helium 5.5 at a flow rate of 1.2 mL min<sup>-1</sup>. Under such conditions, fipronil and its degradation products (compounds **II** and **III**) were identified by their retention times on the chromatograms obtained in single-ion mode (SIM) with characteristic *m/z* ions, as presented in Table 2.

**Fipronil Hydrolysis Study.** Hydrolysis experiments were conducted in duplicate using 2.5 mg L<sup>-1</sup> ( $5.7 \times 10^{-6}$  mol L<sup>-1</sup>) aqueous solutions (2.5% methanol in water), kept in the dark and frequently shaken. To evaluate the influence of pH on the degradation of fipronil, tests were carried out at room

**Table 2. HPLC and GC Retention Times and Mass Spectral and UV-Visible Data for Fipronil and Degradation Products (II–IV)**

compound (mol wt)	chromatography <sup>a</sup> ( <i>t<sub>r</sub></i> , min)		MS, <i>m/z</i> (uma) (rel abundance, %)	UV-vis <sup>b</sup>	
	GC/MS	HPLC		$\lambda$ (nm)	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )
fipronil C <sub>12</sub> H <sub>4</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>4</sub> O <sub>5</sub> (437)	8.8 $\pm$ 0.2	12.9 $\pm$ 0.4	367 [M <sup>+</sup> - CF <sub>3</sub> ] (100) 351 [M <sup>+</sup> - CF <sub>3</sub> - O] (13) 255 [C <sub>6</sub> H <sub>2</sub> (Cl) <sub>2</sub> (CF <sub>3</sub> )(NCH <sub>2</sub> NH <sub>2</sub> )] <sup>+</sup> (14) 213 [M <sup>+</sup> - C <sub>3</sub> N <sub>2</sub> (CN)(F <sub>3</sub> CSO)(NH <sub>2</sub> )] (40) 69 [CF <sub>3</sub> ] <sup>+</sup> (16) other ions: 178 (10), 143 (9), 77 (19)	209 220 280	35000 $\pm$ 5000 28000 $\pm$ 8000 9000 $\pm$ 1000
<b>II</b> C <sub>12</sub> H <sub>6</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>4</sub> O <sub>2</sub> S (455)	17.5 $\pm$ 0.2	7.3 $\pm$ 0.7	385 [M <sup>+</sup> - CF <sub>3</sub> ] (100) 255 [C <sub>6</sub> H <sub>2</sub> (Cl) <sub>2</sub> (CF <sub>3</sub> )(NCH <sub>2</sub> NH <sub>2</sub> )] <sup>+</sup> (42) 213 [M <sup>+</sup> - C <sub>3</sub> N <sub>2</sub> (CONH <sub>2</sub> )(F <sub>3</sub> CSO)(NH <sub>2</sub> )] (26) 69 [CF <sub>3</sub> ] <sup>+</sup> (27)	203 278	71000 $\pm$ 10000 7000 $\pm$ 1000
<b>III</b> C <sub>12</sub> H <sub>4</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>4</sub> (389)	7.4 $\pm$ 0.2	14.4 $\pm$ 0.4	388 [M <sup>+</sup> ] (100) 369 [M <sup>+</sup> - F] (19) 333 [M <sup>+</sup> - F <sub>3</sub> ] (79) 278 [M <sup>+</sup> - CF <sub>3</sub> - CN - NH <sub>2</sub> ] (6) 213 [M <sup>+</sup> - C <sub>3</sub> N <sub>2</sub> (CF <sub>3</sub> )(CN)(NH <sub>2</sub> )] (28) 69 [CF <sub>3</sub> ] <sup>+</sup> (13) other ions: 231 (9), 194 (9), 179 (19), 143 (12), 90 (7), 77 (27)	206 280	35000 $\pm$ 4000 5000 $\pm$ 1000
<b>IV</b> C <sub>11</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>3</sub> N <sub>4</sub> O <sub>3</sub> S (401)		6.2 $\pm$ 0.4		206 277	41000 $\pm$ 9000 6000 $\pm$ 1000

<sup>a</sup> See Materials and Methods for chromatographic conditions. <sup>b</sup> In a mixture of H<sub>2</sub>O/MeOH (90:10 v/v).

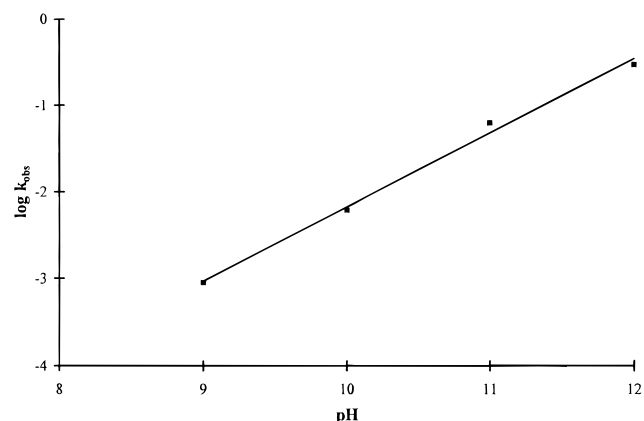
**Table 3. Determination of Observed Rate Constant ( $K_{\text{obs}}$ ) and Half-Life ( $t_{1/2}$ ) for the Hydrolysis of Fipronil under Alkaline Conditions and the Photolysis of Adsorbed Fipronil under a Xenon Lamp**

	Hydrolysis Study				
	$K_{\text{obs}}$ ( $\text{h}^{-1}$ )	$r^2$	$t_{1/2}$ (h)		
pH <sup>a</sup>					
9.0 ± 0.1	0.0009	0.988	770		
10.0 ± 0.1	0.0061	0.982	114		
11.0 ± 0.1	0.062	0.993	11		
12.0 ± 0.1	0.29	0.998	2.4		
temp <sup>b</sup> (°C)					
30 ± 1	0.0093	0.994	75		
37 ± 1	0.016	0.997	43		
45 ± 1	0.039	0.983	18		
Photolysis Study					
	pH	OM <sup>d</sup> (%)	$K_{\text{obs}}$ ( $\text{h}^{-1}$ )	$r^2$	$t_{1/2}$ (h)
soil type <sup>c</sup>					
Saguaia	5.3	0.1	0.0047	0.989	147
Banizombou	5.8	0.3	0.0039	0.988	178
Montpellier	8.3	6.5	0.0032	0.991	217

<sup>a</sup> Hydrolysis of fipronil in aqueous solution ( $C_0 = 5.7 \times 10^{-6}$  mol L<sup>-1</sup>) at ambient temperature ( $22 \pm 2$  °C), in the dark.

<sup>b</sup> Hydrolysis of fipronil in aqueous solution ( $C_0 = 5.7 \times 10^{-6}$  mol L<sup>-1</sup>) at pH 10.0 ± 0.1, in the dark. <sup>c</sup> Irradiation of soil samples ( $5.7 \times 10^{-6}$  mol kg<sup>-1</sup>) in a Suntest solar simulator (xenon lamp).

<sup>d</sup> Organic matter.

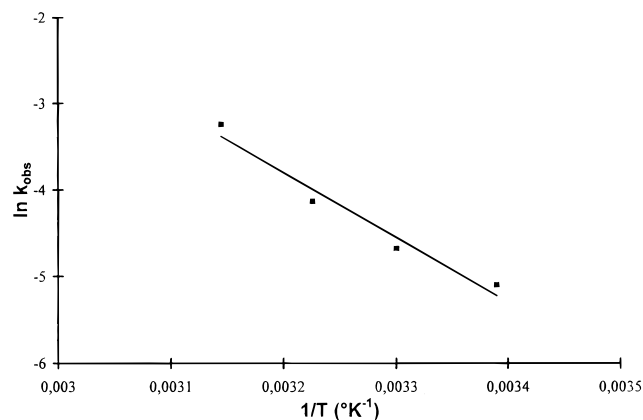


**Figure 1.** Variation of  $\log K_{\text{obs}}$  with pH for the alkaline hydrolysis of fipronil in aqueous solution in the dark at ambient temperature ( $22 \pm 2$  °C).

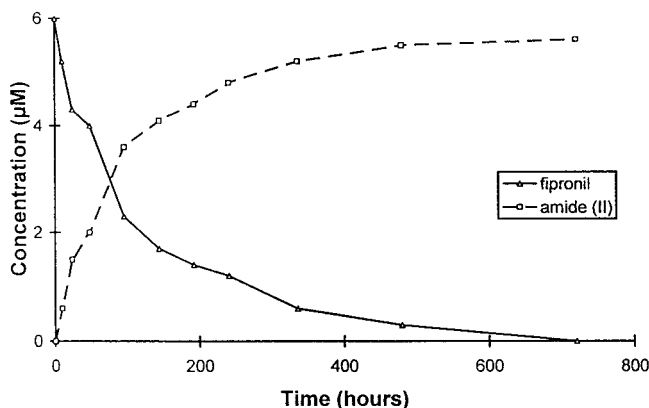
temperature ( $22 \pm 2$  °C) at different values of pH (5.5, 7.0, 9.0, 10.0, 11.0, and  $12.0 \pm 0.1$ ) adjusted using 0.2–1 M NaOH or 0.2–1 M HCl aqueous solutions. According to Rhône-Poulenc (1996), the solubility of the product did not depend on pH: 2.4 mg L<sup>-1</sup> at pH 5.0; 1.9 mg L<sup>-1</sup> at pH 9.0. Aliquots (10 mL) were taken at predetermined times depending on the operating conditions: 0–20 h (pH 12.0), 0–100 h (pH 11.0), 0–500 h (pH 10.0), and 0–2500 h (pH 9, 7, and 5.5). The influence of temperature on the rate of hydrolysis was also examined on aqueous fipronil solutions adjusted to pH 10.0 ± 0.1, maintained on a water bath at temperatures of  $30 \pm 1$  °C and  $37 \pm 1$  °C (0–250 h) and  $45 \pm 1$  °C (0–80 h).

**Fipronil Photolysis Study. Aqueous Phase.** Ten milliliter samples of an aqueous solution (2.5% methanol in water) of fipronil at 2.5 mg L<sup>-1</sup> ( $5.7 \times 10^{-6}$  mol L<sup>-1</sup>) adjusted to pH 5.5 were placed in the quartz capsule of a Suntest solar simulator and irradiated. Irradiation times were 0, 1, 2, 3, 4, 6, 14, 18, and 24 h.

**Adsorbed Phase.** Twenty gram of dry soil was placed in a 500 mL round-bottom flask, and 2 mL of methanolic fipronil solution at 25 mg L<sup>-1</sup> and 50 mL of methanol were added. The suspension was then magnetically stirred for 30 min. Next, the solvent was removed under vacuum at a temperature  $\leq 40$  °C and the soil dried in the open for 1 h. This procedure gives



**Figure 2.** Variation of  $\ln K_{\text{obs}}$  with temperature for the alkaline hydrolysis of fipronil (pH  $10.0 \pm 0.1$ ).



**Figure 3.** Hydrolysis of fipronil at alkaline pH ( $10.0 \pm 0.1$ ) at ambient temperature ( $22 \pm 2$  °C) in the dark: formation of amide derivative (compound II).

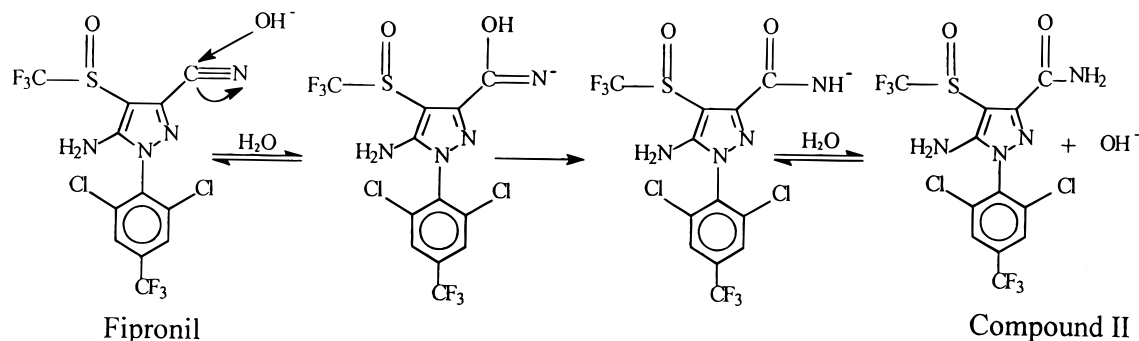
a uniform distribution of fipronil in the soil at a concentration of 2.5 mg kg<sup>-1</sup> ( $5.7 \times 10^{-6}$  mol kg<sup>-1</sup>). Samples (1 g) of this soil were irradiated in quartz capsules for 0, 7, 15, 24, 48, 96, 144, or 196 h. Irradiated samples were kept in the dark at  $-22$  °C until analysis. To verify that the observed degradation was due only to photolysis, the experiment was repeated without irradiation on the three soils kept in the dark for 8 days. All experiments were performed in duplicate.

**Analytical Procedure.** In aqueous solutions, the decrease of fipronil concentrations during hydrolysis and photolysis, as well as the concomitant increase of degradation products, could be followed by direct injection of the aqueous solution into the HPLC system. Identification and analysis were performed using authentic standards for comparison. Limits of quantitation were evaluated at 0.05 mg L<sup>-1</sup> for fipronil and compound III and at 0.03 mg L<sup>-1</sup> for compounds II and IV.

To confirm the results on products I, II, and III by GC/MS, an extraction procedure was set up: fipronil, amide (II), and desulfinyl photolyte (III) were extracted using SPE reversed phase octadecyl (C<sub>18</sub>) cartridges. The cartridge was first conditioned with 5 mL of methanol, followed by 5 mL of pure water, before loading with a 10 mL aliquot of aqueous solution. Elution of 80% of the amide (II) and >90% of fipronil and desulfinyl photolyte (III) was obtained with 5 mL of toluene. This eluate could be concentrated to 1–2 mL under a gentle stream of nitrogen before being analyzed directly by GC/MS.

The solid-phase extraction of fipronil and its photodegradation products was carried out on irradiated soil. One gram soil samples were extracted with  $2 \times 20$  mL of acetonitrile/acetone (70:30 v/v) with magnetic stirring ( $2 \times 30$  min.). The organic phase was filtered under vacuum on a glass fiber filter, dried over anhydrous sodium sulfate, and evaporated under vacuum at a temperature  $\leq 40$  °C. The crude extract was taken up into 0.5–1 mL of toluene, which was injected directly





**Figure 4.** Hydrolysis reaction mechanism of fipronil in alkaline solution.

into the GC/MS system. Extraction recovery rates were determined:  $85 \pm 3\%$  for fipronil,  $90 \pm 5\%$  for the desulfinyl photolyte (**III**), and  $96 \pm 8\%$  for the amide (**II**). The acid (**IV**) was analyzed by HPLC after transfer into 2 mL of redistilled water (recovery rate =  $85 \pm 10\%$ ).

## RESULTS AND DISCUSSION

**Hydrolysis of Fipronil.** The degradation of fipronil in aqueous solution in the absence of light at ambient temperature ( $22^\circ \pm 2^\circ\text{C}$ ) was monitored at different pH values. Fipronil was stable in acid ( $\text{pH } 5.5 \pm 0.1$ ) and neutral ( $\text{pH } 7.0 \pm 0.1$ ) solutions, 80% remaining unchanged after 100 days in both cases. Under alkaline conditions ( $\text{pH } 9.0\text{--}12.0$ ), degradation increased in direct proportion to increase in pH. Representation of the rate of degradation over time can be given by a mathematical model illustrating pseudo-first-order transformation kinetics (Atkins, 1994)

$$C = C_0 e^{-K_{\text{obs}}t} \quad (1)$$

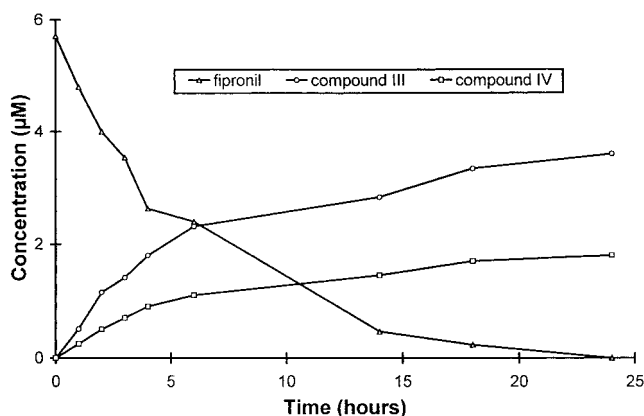
where  $C$  = concentration of fipronil aqueous solution ( $\text{mol L}^{-1}$ ),  $t$  = incubation time (hours),  $C_0$  = initial concentration of fipronil aqueous solution ( $\text{mol L}^{-1}$ ), and  $K_{\text{obs}}$  = fipronil hydrolysis rate constant ( $\text{h}^{-1}$ ). The observed rate constants ( $K_{\text{obs}}$ ) and calculated half-lives ( $t_{1/2}$ ) are given in Table 3. At  $\text{pH } 12.0 \pm 0.1$ , fipronil degradation was 300 times faster than at  $\text{pH } 9.0 \pm 0.1$ , the  $t_{1/2}$  values being, respectively, 2.4 and 770 h.

The experimental results fitted well with a pseudo-first-order hydrolysis of fipronil. For the range of pH from 9 to 12.0, the graph of the logarithm of observed rate constant ( $\log K_{\text{obs}}$ ) versus pH (Figure 1) was linear, with a gradient close to 1 ( $0.85$ ,  $r^2 = 0.995$ ). The fipronil hydrolysis reaction was first-order with respect to the hydroxyl ion,  $K_{\text{obs}} = K_{\text{OH}}(\text{OH}^-)$ .

At temperatures of 22, 30, 37, and  $45^\circ\text{C}$ , the half-lives were, respectively, 114, 75, 43, and 18 h. From the rate constants (Table 3) determined at these four temperatures, the activation energy ( $E_a$ ) of the hydrolysis reaction at  $\text{pH } 10.0 \pm 0.1$  was calculated according to Arrhenius' law

$$K_{\text{obs}} = A e^{-E_a/RT} \quad (2)$$

where  $K_{\text{obs}}$  = fipronil hydrolysis rate constant ( $\text{h}^{-1}$ ),  $A$  = constant characteristic of the fipronil hydrolysis reaction,  $R$  = gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  = temperature (K), and  $E_a$  = activation energy ( $\text{J mol}^{-1}$ ). Figure 2 represents the graph  $\ln K_{\text{obs}} = f(1/T)$ , which gave an activation energy of  $62 \pm 5 \text{ kJ mol}^{-1}$  ( $r^2 = 0.970$ ). The entropy ( $\Delta S$ ) was also determined. The negative sign of the entropy ( $-32.0 \pm 2.0 \text{ J mol}^{-1}$ )



**Figure 5.** Direct photodegradation of fipronil in aqueous solution ( $\text{pH } 5.5$ ): irradiation by xenon lamp (Suntest solar simulator).

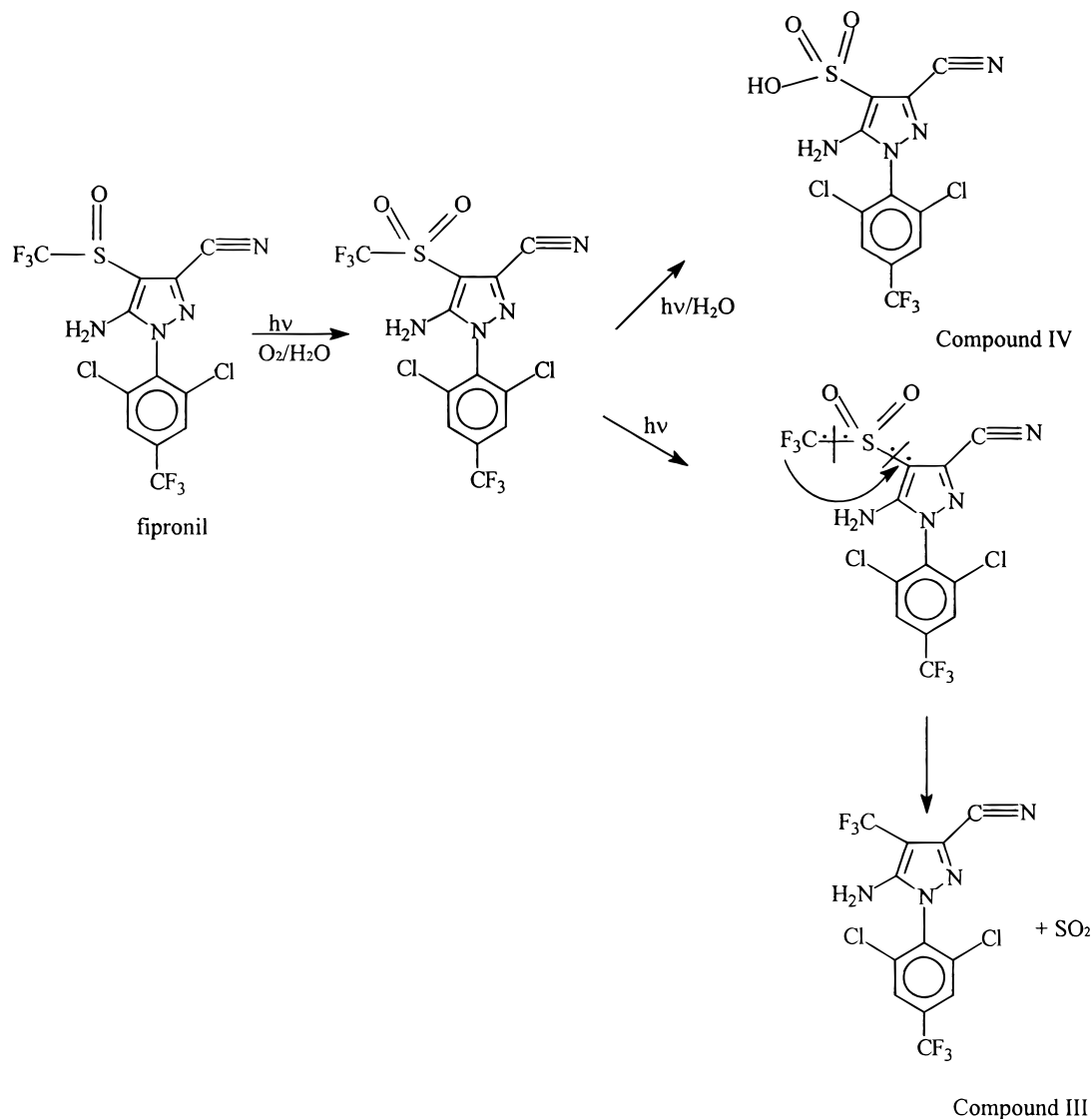
confirmed the loss of degrees of freedom of the hydroxyl ion in the transition state.

The hydrolysis of fipronil in alkaline solution led to a decrease in the concentration of fipronil and a corresponding increase in the concentration of the amide derivative (**II**) (Figure 3), identified from its retention time in different chromatographic systems (HPLC/UV and GC/MS) and its mass spectrum (ions  $m/z$  385, 255, and 213  $\text{uma}$ ) (Table 2). After 1 month, 94% of fipronil had been transformed into compound **II**.

The results of the kinetic studies—absence of general acid–base catalysis, first-order relative to hydroxyl ion, negative entropy—suggest a reaction mechanism involving nucleophilic addition of the hydroxyl ion to a polar nitrile bond of fipronil, yielding an unstable hydroxyimine that undergoes total tautomerization into the corresponding amide (Figure 4).

**Photolysis of Fipronil in Aqueous Solution.** This study was carried out at  $\text{pH } 5.5$  since at this pH fipronil is stable to hydrolysis ( $>95\%$  unchanged after 24 h). Moreover, this pH corresponds to that of the Sahelian soils used subsequently for the study of photolysis in the solid phase. With direct excitation in aqueous solution ( $\text{pH } 5.5$ ), fipronil degraded rapidly with first-order reaction kinetics ( $r^2 = 0.995$ ). The observed rate constant was  $0.17 \pm 0.01 \text{ h}^{-1}$ , and the calculated half-life was 4.1 h. Rigorously, this rate constant corresponds to the sum of the photolysis ( $K_p = 0.168 \text{ h}^{-1}$ ) and hydrolysis ( $K_d \leq 2.15 \cdot 10^{-3} \text{ h}^{-1}$ ) rate constants, but the latter can be discounted.

The primary photodegradation of fipronil in aqueous solution is presented in Figure 5 with the concomitant appearance and evolution of two different compounds by simultaneous reactions. One compound had a reten-



**Figure 6.** Possible photolysis reaction mechanism of fipronil in aqueous solution (pH 5.5): irradiation by xenon lamp (Suntest solar simulator).

tion time in HPLC similar to that of the reference derivative trifluoromethylpyrazole (**III**). Identification was confirmed by GC/MS (ions  $m/z$  388, 369, and 333  $u$ ) (Table 2). The other compound was identified by HPLC retention time as being the pyrazole-4-sulfonic acid derivative (**IV**). Quantitative assessment of the degradation of fipronil and the appearance of the photodegradation products gave consistent results at all incubation times, showing 82–103% of fipronil being transformed into compounds **III** and **IV**. The degradation processes observed in this study were therefore desulfonation and oxidation, but other mechanisms of probable radical nature were not elucidated. We present, however, in Figure 6 a reaction mechanism (theoretical) that appears to us a possibility for the phototransformation of fipronil into products **III** and **IV**, although we were unable to demonstrate passage via the sulfone derivative. This derivative is a degradation product of fipronil which was isolated under other conditions (absence of light), in particular, during the metabolism of fipronil in soil (Bobé et al., 1998).

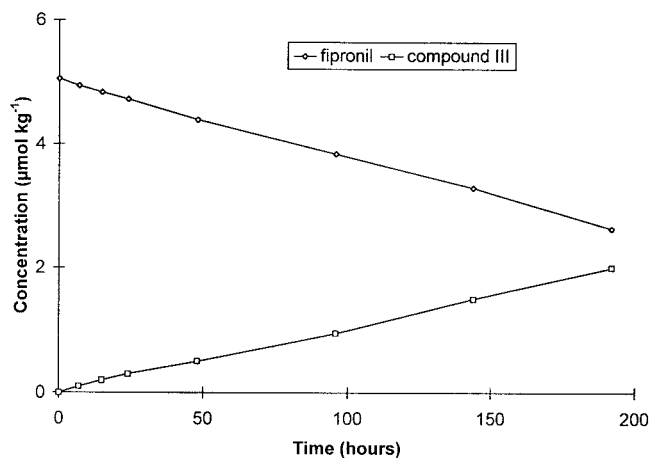
We applied the same kinetic model to the parallel degradation reactions (Frost and Pearson, 1961)

$$C_3 = C_0(K_3/K_{\text{obs}})(1 - e^{-K_{\text{obs}}t}) \quad (3)$$

$$C_4 = C_0(K_4/K_{\text{obs}})(1 - e^{-K_{\text{obs}}t}) \quad (4)$$

where  $C_0$  = initial concentration of fipronil,  $C_3$  and  $C_4$  were the concentrations of compounds **III** and **IV**, respectively,  $t$  = time (h),  $K_{\text{obs}}$  = rate of disappearance of fipronil, and  $K_{\text{obs}} = K_3 + K_4$ , where  $K_3$  and  $K_4$  are the rate constants of the two single steps of the parallel process. Initial concentrations of **III** and **IV** were zero. Their appearance followed first-order kinetics, the concentration of both compounds at any given time being proportional to their respective rate constants, such that  $C_3/C_4 = K_3/K_4$ . The major photolyte (**III**) was the most rapidly formed. The experimental formation rate constants were  $0.11 \pm 0.01 \text{ h}^{-1}$  for the trifluoropyrazole derivative (**III**) and  $0.05 \pm 0.01 \text{ h}^{-1}$  for the pyrazole-4-sulfonic acid derivative (compound **IV**). The correlation coefficients  $r^2$  were 0.979 (compound **III**) and 0.988 (compound **IV**).

**Photolysis of Fipronil in the Solid Phase.** No fipronil degradation occurred in the dark since >90% of the fipronil applied was recovered unchanged after 96 h. Under xenon light, however, degradation occurred



**Figure 7.** Photodegradation of fipronil at the surface of Montpellier soil: irradiation by xenon lamp (Suntest solar simulator).

following first-order kinetics with a correlation coefficient  $r^2 \geq 0.984$ . Rate constants and half-life values for fipronil degradation on different soils are given in Table 3.

In the solid phase, the half-life times observed were greater than those obtained in solution; the slow degradation of fipronil in the solid phase could have been due to a light-shielding effect (Oliver et al., 1979). The rate of degradation seemed to be dependent on the nature of the soil. The maximum rate was observed with Saguia soil and the minimum with Montpellier soil. In this case, the difference in rate constants seems to present a possible correlation with the Freundlich adsorption coefficients ( $K_f$ ) of fipronil determined on each of the soils: 4.3, 7.3, and 45.5 for Saguia, Bani-zoumbou, and Montpellier, respectively (Bobé et al., 1997). Several authors (Yokley et al., 1986; Herbert and Miller, 1990; Nag and Dureja, 1996) have previously described the influence of the adsorption capacity of the soil on the availability of the product subjected to photolysis. The photodegradation study on the three soils revealed only one photolyte, compound III (Figure 7). Compound IV, previously found in the photodegradation study on aqueous solutions, was not detected under these conditions.

**Conclusion.** The hydrolysis and photolysis studies carried out on fipronil in aqueous solution and/or on soil surfaces have enabled us to better understand the behavior of this insecticide in the environment. In September 1995, we undertook a plain field study on two acid soils under Sahelian conditions—Banizoumbou (pH 5.8) and Saguia (pH 5.3). The results obtained show that various metabolites are formed over time, notably the amide derivative (II). The formation of this compound in the two soils revealed a period of latency. This suggests a biological rather than a chemical hydrolysis. The results of the hydrolysis studies in aqueous solution seem to confirm this hypothesis: fipronil degrades to the amide derivative at high pH (9.0–12.0) but is stable at pH 5.5, degradation not exceeding 20% after 100 days.

Photolysis of fipronil in aqueous solution under a xenon lamp in a Suntest solar simulator revealed two parallel photodegradation reactions with the appearance of the trifluoromethylpyrazole derivative (III) and the pyrazole-4-sulfonic acid derivative (IV). The reaction mechanisms, probably radical in nature, were not elucidated. The photodegradation studies on soil surfaces, under the same operating conditions, revealed the formation of the trifluoromethylpyrazole derivative (III). During the plain field study on Sahelian soils, this photolyte appeared rapidly during the first few days in a manner concomitant with the degradation of fipronil. The photolytic reaction was intense as long as the fipronil was not protected from the light by the solid soil matrix. Moreover, the study of fipronil photolysis at the surface of the three soils studied clearly demonstrated that the screening effect of soil particles and the adsorption of fipronil by the soil reduced the intensity of the photodegradation.

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