

Nicosulfuron: Alcoholysis, Chemical Hydrolysis, and Degradation on Various Minerals

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Alcoholysis (methanol or ethanol) and hydrolysis (pH ranging from 4 to 11) of the herbicide nicosulfuron at 30 °C principally involves the breakdown of the urea part of the molecule. A high yield of the corresponding carbamate was obtained along with aminopyrimidine during alcoholysis. Hydrolysis led to both aminopyrimidine and pyridylsulfonamide. The latter compound may be easily cyclized (pH \geq 7). First-order kinetics describe the rates of alcoholysis and hydrolysis well. The rate constants (0.44 days⁻¹ for methanolysis) decreased from 0.50 to 0.002 days⁻¹ as pH increased from 4 to 8, then remained stable under alkaline conditions. In acidic or neutral solution, the hydrolysis path appeared prevalent (\geq 70%), whereas in an alkaline medium it decreased when pH increased. The chemical degradation of nicosulfuron on various dry minerals (calcium bentonite, kaolinite, silica gel, H⁺ bentonite, montmorillonite K10, and alumina) was investigated at 30 °C. The best conditions for the degradation are obtained on acidic minerals after herbicide deposition using the liquid method. Under these conditions an acceptable correlation with pseudo-first-order kinetics was observed, and the major degradation path is similar to that proposed for chemical hydrolysis. Conversely, alumina seemed to favor other unknown degradation processes. The hydrolysis paths of nicosulfuron and rimsulfuron appeared to be different.

KEYWORDS: Nicosulfuron; alcoholysis; hydrolysis; degradation

INTRODUCTION

Nicosulfuron is a sulfonylurea herbicide developed by DuPont (Accent) that has been used successfully for weed control in corn (1). Because of its chemical structure, 1-(4,6-dimethoxy-pyrimidin-2-yl)-3-(3-dimethylcarbamoyl-2-pyridylsulfonyl)-urea, which exhibits a pyridyl-sulfonylurea bridge in place of the usual phenyl-sulfonylurea, nicosulfuron **1** (Figure 1) belongs to the substituted pyridinesulfonylurea group that also includes herbicides such as rimsulfuron, flupyr-sulfuron-methyl, and flazasulfuron. The pyridylsulfonylurea structure of these herbicides provides interesting structure–activity relationships (2, 3).

The metabolic pathways of some sulfonylurea herbicides in crops were previously reviewed by Koeppe and Brown (4). Although the pyrimidine portion of nicosulfuron is identical to that of rimsulfuron and differs only by the substitution at the position 3 of the pyridine ring, nicosulfuron does not undergo the unusual bridge contraction described for rimsulfuron in maize. This same unexpected sulfonylurea bridge contraction also appeared as the major degradation path during rimsulfuron hydrolysis (5–7), or during its degradation on clays (8) and in soils (9, 10). Moreover, a comparable bridge contraction was described for flupyr-sulfuron-methyl (11, 12).

Nevertheless, very few studies have been published on the hydrolysis and degradation of nicosulfuron in soils. Although hydrolysis rate constants measured by Berger and Wolfe (13)

appeared comparable with chlorsulfuron, no degradation pathway was suggested. Ukrainczyk and Rashid (14) observed an unexpectedly strong, irreversible sorption of nicosulfuron on negatively charged clay surfaces. These authors suggested two possible explanations: either nicosulfuron is present in solution as a zwitterion, or its rapid hydrolysis is catalyzed by the minerals' surface acidity. Consequently, the transport and mobility of this herbicide in soil was evaluated; nicosulfuron may be less likely to leach into groundwater than other sulfonylurea herbicides (15, 16).

The aim of this study was to investigate the alcoholysis, chemical hydrolysis, and behavior on minerals of nicosulfuron in order to determine its major degradation path. The results were compared with those described for other pyridylsulfonylurea herbicides.

MATERIALS AND METHODS

Chemicals. Nicosulfuron **1** was a gift from DuPont Agricultural Products (France), and 2-amino-4,6-dimethoxypyrimidine **2** was obtained from Aldrich.

3-Dimethylcarbamoyl-2-pyridylsulfonamide 3. Nicosulfuron (500 mg) in 50 mL of water was maintained at 70 °C for 5 h. The aminopyrimidine formed was then extracted with diethyl ether (4 \times 20 mL) and discarded. The aqueous solution was evaporated under vacuum to dryness. Recrystallization was carried out in ethanol, and a high-purity, white, crystalline powder was obtained: yield 80%; mp 186 °C.

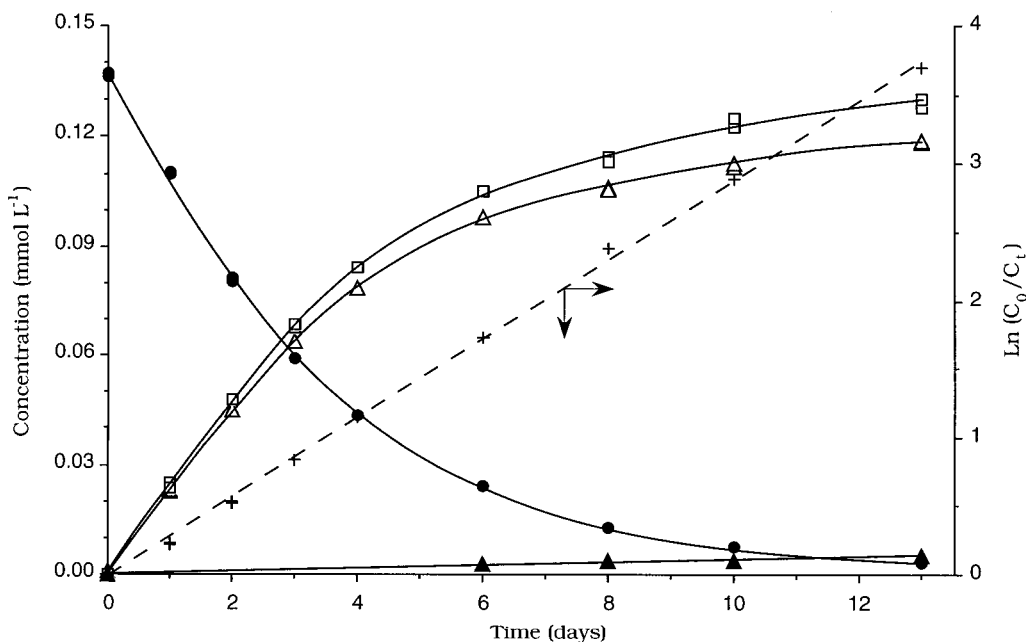


Figure 2. Alcoholysis of nicosulfuron in ethyl alcohol at 30 °C. Concentration of nicosulfuron **1** (●), ethylcarbamate **4** (□), aminopyrimidine **2** (Δ), and pyridylsulfonamide **3** (▲) as a function of time. First-order kinetic line was established from the loss of nicosulfuron (-+-).

Table 1. Alcoholysis of Nicosulfuron at 30 °C

	alcohol (R-OH)	
	CH ₃ OH	C ₂ H ₅ OH
rate constants (days ⁻¹) ^a	0.44	0.29
relative selectivity (%) ^b	97	96

^a Rate constants were determined assuming first-order kinetics. ^b Relative selectivity measured the percentage of observed alcoholysis.

analysis of crude alcoholic samples provoked a weak failure (<10%) for the dosage of aminopyrimidine **2** as shown in **Figure 2**.

Hydrolysis Rates. Nicosulfuron hydrolysis experiments were conducted at 30 °C in buffered aqueous solutions using a pH ranging from 4 to 11. A very acceptable description was obtained with first-order kinetics (for example, **Figure 4**). An accurate rate constant k (d⁻¹) was established graphically from the results of each hydrolysis experiment; half-lives calculated from the k -values were in excellent agreement with the experimental measurements. The results are presented in **Figure 3**. These data, in good accordance with Berger and Wolfe's results (13), clearly indicate that nicosulfuron hydrolysis was much more rapid under acidic conditions, as was observed with most sulfonylurea herbicides (18, 19). The rate of hydrolysis reached a minimum at pH 8, and then remained stable under alkaline conditions.

Pyridylsulfonamide **3** may be cyclized to the derivative **6** (**Figure 1**); this transformation appears to be pH sensitive, i.e., insignificant below pH 7, and fairly high between pH 7 and 11 (**Figure 3**). A buffer effect could explain the unexpected maximum observed around pH 9.

Transformation Pathway of Hydrolysis. The chemical hydrolysis pathway of nicosulfuron described in **Figure 1** involves two different paths: (a) Hydrolysis of the sulfonylurea bridge of the herbicide molecule to form aminopyrimidine **2**, which remains stable (20), and pyridylsulfonamide **3**, which becomes cyclized if the conditions are appropriate (pH ≥ 7). This proved to be the major degradation path; and (b) Formation

of some unknown compounds which appeared in amounts too small to be identified. However, contraction of the sulfonylurea bridge could be envisaged as previously described for other pyridylsulfonylurea herbicides such as rimsulfuron (5, 10, 21, 22) or flupyralsulfuron-methyl (12, 23).

The nicosulfuron degradation curves observed at pH 5 are presented in **Figure 4**. The selectivity for hydrolysis (sulfonylurea bridge breakdown) was established, throughout the transformation, by comparing the quantity of aminopyrimidine produced with the quantity of nicosulfuron consumed. **Figure 3** shows the results obtained. In neutral or acidic solution, the hydrolysis path remained prevalent (≥70%), whereas in an alkaline medium it decreased as pH increased.

Degradation on Various Dry Minerals. The minerals used in this study were selected to represent a wide range of surface properties. If calcium bentonite appeared fairly neutral, superficial acidity remained weak for kaolinite, moderate for silica gel, and strong for H⁺ bentonite and montmorillonite K10. Conversely, a weakly basic character was observed with alumina. Although most sulfonylurea herbicides, which are weak acids, exhibited only a limited affinity for various minerals as described previously for chlorsulfuron (24) or primisulfuron (25), nicosulfuron (pK_a = 4.3) showed an unexpectedly strong interaction with clay minerals (14). This could explain why the amount of nicosulfuron initially recovered from mineral samples was generally lower than expected (**Table 2**), despite the use of the B₁ extraction system (water/ACOH/CHCl₃). Nevertheless, this same system proved very effective in the presence of chlorimuron-ethyl, a herbicide with an equivalent pK_a of 4.2 (26). Other extraction procedures (B₂ or B₃) appeared less satisfactory. However, the initial recovery of nicosulfuron also depended on the method used to deposit the herbicide. A better extraction rate was obtained after deposition by the dry method (thorough crushing of the powder mixture) which led to a fairly crude dispersion of the herbicide particles, unfavorable to interaction with the mineral surface. Conversely, the liquid method (herbicide dissolution in acetone, then evaporation to dryness of the mineral suspension) gave a homogeneous layer of herbicide on the mineral surface that promoted its adsorption

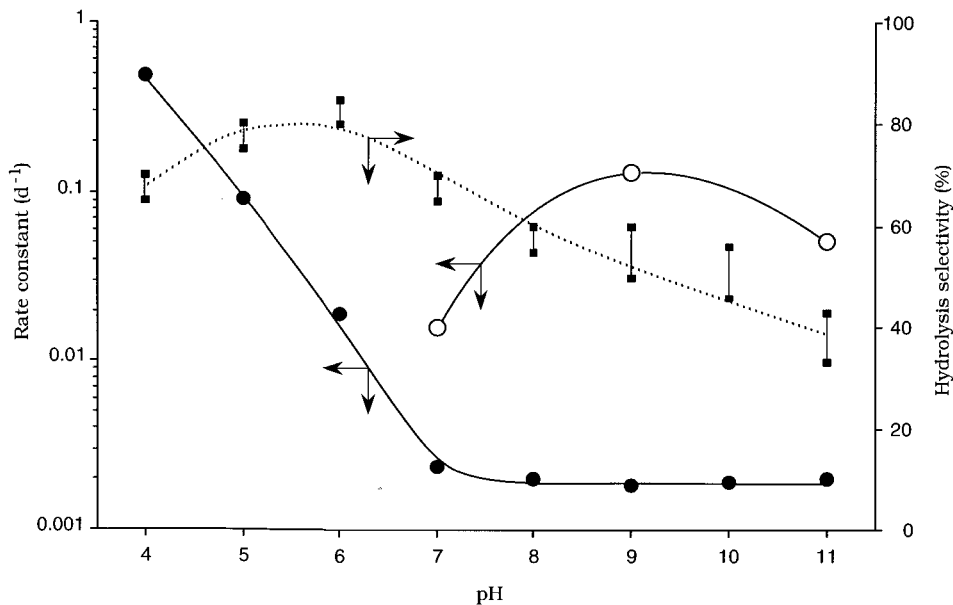


Figure 3. Hydrolysis rate constants at 30 °C of nicosulfuron 1 (●) and pyridylsulfonamide 3 (○), selectivity (%) for hydrolysis pathway (---) as a function of pH.

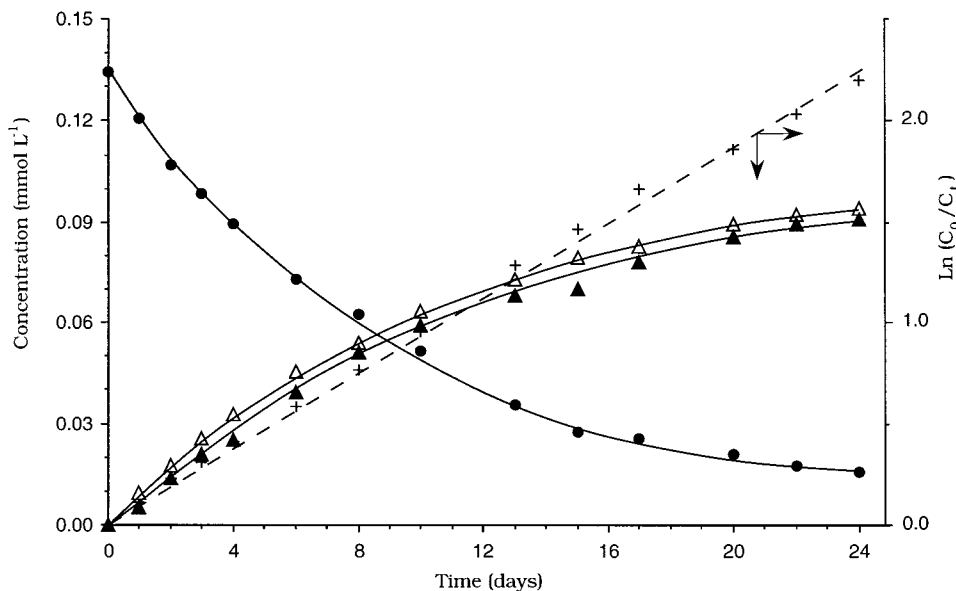


Figure 4. Hydrolysis of nicosulfuron in an aqueous buffer solution at pH 5 and 30 °C. Concentration of nicosulfuron 1 (●), aminopyrimidine 2 (Δ), and pyridylsulfonamide 3 (▲) as a function of time. First-order kinetic line was established from the loss of nicosulfuron (-+-).

but reduced its extraction rate. The lower values (Table 2) observed on acidic minerals (silica gel, H⁺ bentonite, and montmorillonite K10) probably indicate a stronger herbicide adsorption; similar observations were previously described for chlorimuron-ethyl and bensulfuron-methyl (26, 27).

These minerals did not provoke the expected rapid degradation, catalyzed by clay surface, suggested by Ukrainczyk and Rashid (14). The measured half-lives (Table 2) appeared close enough to those described for bensulfuron-methyl (27) and were always higher than those for chlorimuron ethyl under the same conditions (26). The liquid deposition method always favored higher degradation rates over acidic selected minerals (silica gel, H⁺ bentonite, and montmorillonite K10) and gave an acceptable correlation with pseudo-first-order kinetics. Calcium bentonite remained completely inactive.

The degradation of nicosulfuron after deposition on dry minerals follows the same chemical path as that established for

its hydrolysis, shown in Figure 1. Hydrolysis of the sulfonylurea bridge of the herbicide molecule appeared as a major degradation path ($\geq 75\%$) using neutral and acidic minerals (Table 2). Both aminopyrimidine 2 and pyridylsulfonamide 3 were recovered in acceptable concordance (B₃ extraction system) from kaolinite and silica gel (Figure 5). However, in the presence of strongly acidic clays (H⁺ bentonite, montmorillonite K10), only pyridylsulfonamide was extracted (B₂ extraction system) attesting to a strong affinity between aminopyrimidine 2 and the acidic surface as reported previously (27). After deposition of nicosulfuron on alumina (basic surface mineral), the formation of aminopyrimidine 2 in weak yields ($\sim 5\%$) seemed to indicate the limited presence of sulfonylurea bridge hydrolysis while pyridylsulfonamide remained undetected because of its rapid cyclization into compound 5. Although several degradation compounds were detected, it was not possible to identify them.

Table 2. Degradation of Nicosulfuron after Deposition on Various Dry Minerals at 30 °C

minerals	dry deposition method					liquid deposition method				
	nicosulfuron 1			half-life ^b (days)	hydrolysis selectivity ^c (%)	nicosulfuron 1			half-life ^b (days)	hydrolysis selectivity ^c (%)
	initial recovery (%) ^a					initial recovery (%) ^a				
B ₁	B ₂	B ₃	B ₁	B ₂	B ₃	B ₁	B ₂	B ₃		
calcium bentonite	99	25	10	— ^g	—	88	27	4	— ^g	—
kaolinite	88	68	66	≥ 100	75 ^d	90	68	60	78	76 ^d
silica gel	76	72	51	66	90 ^d	65	39	26	32 ^f	85 ^d
H ⁺ bentonite	85	64	2	71	81 ^e	70	66	1	15 ^f	86 ^e
montmorillonite K10	76	69	4	39	90 ^e	55	70	2	12 ^f	90 ^e
alumina	85	58	76	75	9 ^d	83	62	74	55 ^f	9 ^d

^a Three extraction systems were used simultaneously: B₁ (water/AcOH/CHCl₃), B₂ (CH₃OH), and B₃ (AcOH/CHCl₃). ^b Established using B₁ extraction system. ^c Apparent hydrolysis selectivity was measured by comparing the amounts of aminopyrimidine 2 or pyridylsulfonamide 3 formed with the amount of nicosulfuron 1 consumed (B₁ system). ^d Measured from the amount of aminopyrimidine formed (B₃ system). ^e Measured from the amount of pyridylsulfonamide formed (B₂ system). ^f Acceptable correlation with pseudo-first-order kinetics. ^g No degradation detected.

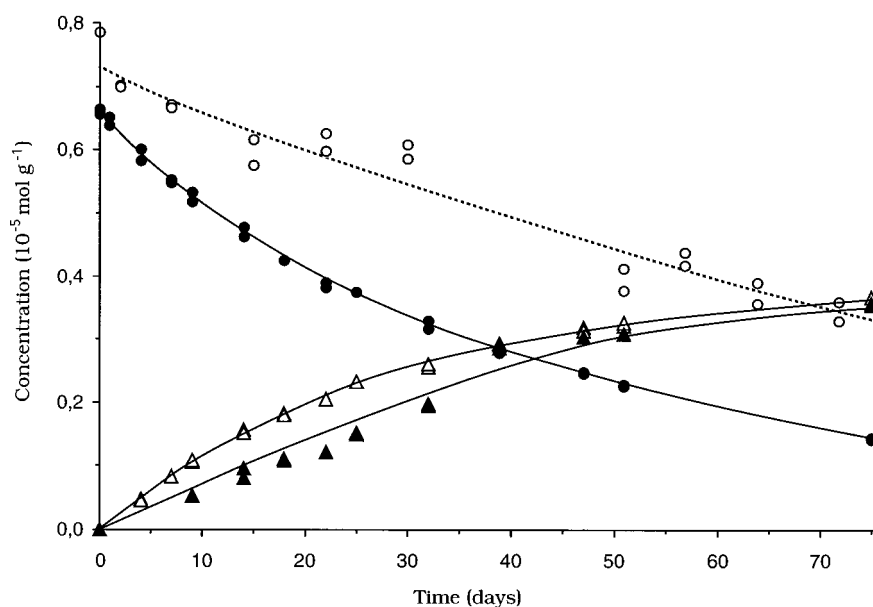


Figure 5. Degradation of nicosulfuron after deposition on dry silica gel powder at 30 °C as a function of time. Concentration of nicosulfuron 1 (●), aminopyrimidine 2 (Δ), and pyridylsulfonamide 3 (▲) observed after liquid deposition. Concentration of nicosulfuron 1 (○) observed after dry deposition.

CONCLUSION

Nicosulfuron 1 belongs to the substituted pyridinesulfonylurea herbicides: the chemical structure of its molecule exhibits a pyridyl-sulfonylurea bridge in place of the usual phenyl-sulfonylurea group. This structural feature did not affect the alcoholysis reaction; the corresponding carbamates 4 (methyl or ethyl) were easily obtained in high yields. With reference to previous studies (17), the alcoholysis reaction appears to be a characteristic of all sulfonylurea herbicides.

As with other sulfonylureas, the pH governs the hydrolysis rate of nicosulfuron. At 30 °C, hydrolysis was much more rapid under acidic conditions; the rate of hydrolysis reached a minimum at pH 8 and then remained stable, in good agreement with Berger and Wolfe's results (13). The hydrolysis reactions were best described by first-order kinetics.

Contrary to all expectations, hydrolysis of the sulfonylurea bridge proved to be the prevalent path of nicosulfuron degradation, whereas bridge contraction was prevalent for similar pyridinesulfonylurea herbicides (rimsulfuron and flupyr-sulfuron-methyl). The principal hydrolysis products are aminopyrimidine 2, which is stable, and pyridylsulfonamide 3, which can be cyclized (pH ≥ 7). The formation of several unknown compounds, which appeared in amounts too small to be identified,

could indicate a few bridge contraction reactions. Additional studies are indicated here.

The rapid hydrolysis of nicosulfuron catalyzed by clay minerals, previously suggested by Ukrainczyk and Rashid (14), seems unlikely. With the exception of calcium bentonite, which was inactive, only slow degradation of this herbicide was observed at 30 °C after its deposition on various oven-dried minerals. Similar observations have been reported for various sulfonylurea herbicides (27). The strong sorption of nicosulfuron on clay surfaces, described earlier (14), generally led to the incomplete initial recovery of the herbicide from mineral samples, despite the use of three different extraction systems. The best conditions for the degradation of nicosulfuron are obtained on acidic minerals after herbicide deposition using the liquid method; acceptable correlation with pseudo-first-order kinetics was then observed.

Hydrolysis of the sulfonylurea bridge of the herbicide molecule also appeared as a major degradation path (≥75%) using neutral and acidic minerals; pyridylsulfonamide 3 was always recovered in good yields, whereas aminopyrimidine 2 remained unrecoverable from strong acid surfaces (H⁺ bentonite and montmorillonite K10). Conversely, the weak basic surface of alumina seemed to favor other unknown degradations.

Nicosulfuron appears quite distinguishable from rimsulfuron or flupyralsulfuron-methyl by its hydrolysis path and by its metabolism in maize previously described by Koeppel and Brown (4). These results encourage us to envisage studying the behavior of flazasulfuron, another pyridylsulfonyleurea herbicide.

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