

## SORPTION OF ISOXAFLUTOLE AND DKN ON ORGANOCCLAYS

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**Abstract**—Sorption of the herbicide isoxaflutole and its main degradate, diketonitrile (DKN), to natural clays, SAZ-1, SWy-2 and SHCa-1, and the organoclay derivatives (octadecylammonium (ODA) and hexadecyltrimethylammonium (HDTMA)) of these clays was investigated. Isoxaflutole hydrolysis to DKN was too rapid in aqueous solutions with organoclays to characterize sorption. No measurable DKN sorption was observed for the natural clays. Sorption of DKN was greater on organoclays with an interlayer paraffin-like complex that were prepared from the high-charge SAZ-1 clay than on organoclays with a bilayer or monolayer interlayer complex prepared using lower-charge SWy-2 or SHCa-1 clays. Desorption isotherms indicated that sorption was irreversible. For SAZ-1 with HDTMA at ~100% of the clay CEC, the  $d_{001}$  values suggest that DKN enters the interlamellar space of the organoclay and dissociates into the anion. The DKN anion forms a very stable chelate complex with the residual cations and/or partially-coordinated structural cations. This strong interaction supports the irreversibility of the sorptive process.

**Key Words**—Degradation, Diketionitrile, Freundlich, Hysteresis, Isoxaflutole, Organoclays, Sorption.

### INTRODUCTION

Isoxaflutole 5-cyclopropyl isoxazol-4-yl-2-mesyl-4-trifluoromethylphenyl ketone is a recently developed herbicide that belongs to a new class of herbicides, isoxazoles (Cain *et al.*, 1993), used for pre-emergence control of grass and broadleaf weeds in corn and sugarcane (Luscombe *et al.*, 1995; Luscombe and Pallet, 1996). Isoxaflutole readily hydrolyzes to a diketonitrile degradation product, DKN, [2-cyclopropyl-3-(2-mesyl-4-trimethylphenyl)-3-oxopropanenitrile] by opening of the isoxazol ring (Pallet *et al.*, 1997). This diketonitrile degradate is herbicidally active, inhibiting a specific enzyme of carotenoid synthesis (*p*-hydroxyphenyl pyruvate dioxygenase, HPPD) (Luscombe *et al.*, 1995; Pallet *et al.*, 1998). Preliminary studies (Rhône-Poulenc Agro, now Bayer CropScience) have shown that isoxaflutole hydrolyzes rapidly to DKN in water, soils and plants.

As a pre-emergence herbicide, isoxaflutole is applied to soils, hence sorption processes are important in determining the fate and behavior of the herbicide in the environment, as it controls other processes such as transport, mobility and degradability (Bailey and White, 1970; Koskinen and Harper, 1990; Calvet, 1989). To date, very limited research has been published on the fate of isoxaflutole in soil. Taylor-Lovell *et al.* (2000) studied hydrolysis and soil sorption of the herbicide isoxaflutole and its DKN degradate. They demonstrated that most (83%) of the isoxaflutole remained in solution after 24 h in a soil-free system, but only 15% remained

in solution in the presence of soil. They also found that isoxaflutole was sorbed, by four soils, to a greater extent than DKN and that sorption of both compounds increased with higher soil organic matter contents. Mitra *et al.* (1999) also showed that sorption of <sup>14</sup>C-isoxaflutole residues (presumably a mixture of isoxaflutole and DKN) was mainly influenced by the organic matter content and pH, but was not influenced appreciably by clay content. In another study, Mitra *et al.* (2000) also showed that DKN had a sorptive behavior similar to that shown for <sup>14</sup>C-isoxaflutole residues, where sorption was mainly influenced by organic matter content. However, it appears that Mitra *et al.* (1999) did not determine whether isoxaflutole hydrolyzed during the experiment. Sorption of isoxaflutole was assumed to be equal to the loss of <sup>14</sup>C from solution. However, if isoxaflutole rapidly decomposed to DKN, then the results would be expected to be similar for both isoxaflutole and DKN.

Soils are heterogeneous systems where all the components are usually intimately associated, therefore individual effects by components on soil processes are difficult to separate. Hence, it is appropriate to evaluate the importance of different individual soil components, such as clays, on pesticide sorption. Smectites, due to their large interlayer surface area and hydration water of exchangeable cations, are good sorbents for polar organic chemicals, but their sorption capacity for hydrophobic organic compounds is low (Mortland, 1970; Hermosin and Cornejo, 1992; Jaynes and Vance, 1996). When exchangeable inorganic cations are replaced by organic cations, the surface properties of the smectites change from hydrophilic to hydrophobic making them highly effective in sorption of hydrophobic

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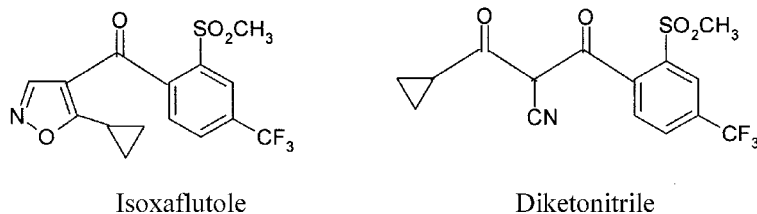


Figure 1. Chemical structures of isoxaflutole and its diketonitrile degradate.

organic compounds (Boyd *et al.*, 1988; Lee *et al.*, 1989; Zhao *et al.*, 1996; Xu *et al.*, 1997; Celis *et al.*, 2000; Cox *et al.*, 2001; Carrizosa *et al.*, 2000, 2001).

The specific objectives of this research, therefore, were to: (1) determine isoxaflutole degradation in the presence of different natural and organo-clays; (2) determine the potential of natural and organic cation-exchanged clays to act as sorbents for DKN, the herbicidally-active degradation product of isoxaflutole; (3) examine the reversibility of DKN sorption to clays; and (4) to determine the possible interaction mechanisms involved in the sorption process using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy.

## MATERIALS AND METHODS

### Chemicals

Pure analytical standard isoxaflutole (chemical purity 98.6%) and DKN (chemical purity 99.9) (Figure 1) were supplied by Rhone-Poulenc Agriculture Ltd (Essex, England). Phenyl- $U-^{14}C$  isoxaflutole (radiochemical purity 99.1%, specific activity = 1550 MBq mmol $^{-1}$ ) and phenyl- $U-^{14}C$  DKN (radiochemical purity 100%, specific activity = 901.1 MBq mmol $^{-1}$ ) were also supplied by Rhone-Poulenc Agriculture Ltd.

### Sorbents

Table 1 summarizes the characteristics of the different sorbents used in this study. The main difference between hectorite (SHCa-1), Wyoming montmorillonite (SWy-2), and Arizona montmorillonite (SAz-1), supplied by the Clay Minerals Repository of The Clay Minerals Society (currently hosted by Purdue University, Indiana), is the density of layer charge in the octahedral sheet, resulting in CEC of 44 cmol $_c$  kg $^{-1}$ , 76 cmol $_c$  kg $^{-1}$  and 120 cmol $_c$  kg $^{-1}$ , for SHCa-1, SWy-2 and SAz-1, respectively (van Olphen and Fripiat, 1979). Two different organic cations, octadecylammonium (ODA) and hexadecyltrimethylammonium (HDTMA) and two different organic cation loadings (~50% and ~100% of the CEC of the clays) were used in the synthesis of the organoclays.

For organoclay synthesis, 100 g of clays were treated with an amount of ethanol:water (50:50) solution containing the amount of alkylammonium chloride equivalent to 50% and 100% of the CEC of the clay as described elsewhere (Carrizosa *et al.*, 2000, 2001). The suspensions were shaken at 20±2°C for 24 h, centrifuged, washed with distilled water until Cl-free, then freeze dried. Organic carbon (OC) and nitrogen in the sorbents were determined using a total elemental carbon, hydrogen, nitrogen and sulfur analyzer (LECO

Table 1. Characteristics of the sorbents.

Sorbent	Mineral phase	Saturation cation	pH	CEC	%OC	%OCSt	$d_{001}$ (nm)
SA	SAz-1	–	6.5	120	–	0	1.5
SW	SWy-2	–	6.5	76	–	0	1.3
SH	SHCa-1	–	6.5	44	–	0	1.1
SA-HDTMA <sub>50</sub>	SAz-1	Hexadecyltrimethylammonium	6.8	120	15.0	54	2.2
SA-HDTMA <sub>100</sub>	SAz-1	Hexadecyltrimethylammonium	6.8	120	22.5	83	2.3
SA-ODA <sub>50</sub>	SAz-1	Octadecylammonium	6.9	120	17.2	67	3.1
SA-ODA <sub>100</sub>	SAz-1	Octadecylammonium	6.9	120	25.5	98	3.2
SW-HDTMA <sub>50</sub>	SWy-2	Hexadecyltrimethylammonium	6.9	76	9.8	56	1.7
SW-HDTMA <sub>100</sub>	SWy-2	Hexadecyltrimethylammonium	6.9	76	14.7	85	1.8
SW-ODA <sub>50</sub>	SWy-2	Octadecylammonium	6.9	76	9.9	60	1.7
SW-ODA <sub>100</sub>	SWy-2	Octadecylammonium	6.9	76	15	90	1.7
SH-HDTMA <sub>50</sub>	SHCa-1	Hexadecyltrimethylammonium	6.6	44	8.6	47	1.4
SH-HDTMA <sub>100</sub>	SHCa-1	Hexadecyltrimethylammonium	6.7	44	13.2	86	1.8
SH-ODA <sub>50</sub>	SHCa-1	Octadecylammonium	6.9	44	10.5	45	1.6
SH-ODA <sub>100</sub>	SHCa-1	Octadecylammonium	6.9	44	12.6	94	1.7

SAz-1, Arizona smectite; SWy-2, SHCa-1, hectorite; Wyoming smectite; CEC, cation exchange capacity; %OC, organic carbon content; %OCSt, organic carbon saturation;  $d_{001}$ , basal spacing

CHNS932). The pH was measured using a combination glass electrode. X-ray diffraction patterns were obtained on oriented specimens with a Siemens D-500 diffractometer (Siemens, Stuttgart, Germany) using CuK $\alpha$  radiation.

#### *Isoxaflutole kinetic studies*

A stock treatment solution was prepared by combining 0.155 mg of  $^{14}\text{C}$ -isoxaflutole with 1000 mL of 0.01 M CaCl $_2$ , giving a final solution radioactivity of  $\sim 4000$  DPM mL $^{-1}$ . In 35 mL glass centrifuge tubes with Teflon-lined caps, 10 mL of the isoxaflutole treatment solution were added to 20 mg of the clays. The tubes were shaken mechanically for 2, 4, 6, 16, 24 and 48 h at 20 $\pm$ 2 $^\circ\text{C}$ . At each sampling time two replicates were removed, and  $^{14}\text{C}$ -containing residues extracted from the clays by shaking for 2 h with 10 mL of acetonitrile (ACN). After the suspensions were centrifuged at 478  $\times$  g (2000 rpm) for 15 min, 1 mL aliquots were removed for analysis. The aliquots were mixed with 5 mL of Ecolite scintillation cocktail and the amount of radioactivity determined by liquid scintillation counting (LSC) using a liquid scintillation analyzer (Packard Instruments Co., Downers Grove, IL). A clay-free solution of isoxaflutole was used as control. The remaining supernatant liquid was saved for later analysis of isoxaflutole and DKN.

In the HPLC/LSC analyses, isoxaflutole and DKN were separated using a Zorbax RX-C8 column (2.1 mm  $\times$  15 cm), on a 1090 Hewlett Packard HPLC operating at room temperature ( $\sim 20\pm 2^\circ\text{C}$ ). The mobile phase was 68% acidified water (0.8% formic acid) and 32% ACN with a flow rate of 1 mL min $^{-1}$ . The injection volume was 100  $\mu\text{L}$ . Detection of isoxaflutole and DKN was determined at 254 nm. According to the retention times of DKN (1.8 min) and isoxaflutole (10.4 min), obtained by injecting the pure analytical standards, HPLC fractions were collected, mixed with liquid scintillation cocktail and  $^{14}\text{C}$ -quantified by LSC.

#### *DKN sorption-desorption experiments*

The DKN sorption isotherms on the different sorbents were obtained by using the batch equilibration technique. Initial DKN solutions were prepared in 0.01 M CaCl $_2$  at concentrations ranging from 3 to 100  $\mu\text{g L}^{-1}$ . Radiolabeled DKN was added to non-radioactive solutions to give a final solution radioactivity of  $\sim 4000$  DPM mL $^{-1}$  (27  $\mu\text{g L}^{-1}$ ). Duplicate 20 mg sorbent samples were equilibrated with 8 mL of DKN initial solution in 35 mL glass centrifuge tubes with Teflon-lined caps by shaking mechanically at 20 $\pm$ 2 $^\circ\text{C}$  for 24 h. Kinetic studies showed that 24 h were enough to reach an apparent sorption equilibrium (unpublished results). After equilibration, the suspensions were centrifuged at 478  $\times$  g (2000 rpm) for 15 min, and the radioactivity of the supernatant liquid determined by LSC. The amount of DKN in solution was calculated from the specific

activity of the initial DKN solution. The supernatant solution remaining was saved for later analysis as previously discussed.

Desorption was measured immediately after sorption from the highest equilibrium concentration point of the sorption isotherms. The 4 mL aliquots of supernatant liquid removed for the sorption analysis were replaced with 4 mL of 0.01 M CaCl $_2$ . After shaking at 20 $\pm$ 2 $^\circ\text{C}$  for 24 h, the suspensions were centrifuged and a 4 mL aliquot of the supernatant liquid was removed for analysis. This desorption cycle was repeated three times. The supernatant liquid remaining was saved for later analysis of DKN as previously discussed.

Sorption and desorption isotherms were fitted to the linearized form of the Freundlich equation,  $\log C_s = \log K_f + 1/n_f \log C_e$ , where  $C_s$  ( $\mu\text{g g}^{-1}$ ) is the amount of DKN sorbed at the equilibrium concentration  $C_e$  ( $\mu\text{g L}^{-1}$ ), and  $K_f$  and  $1/n_f$  are the empirical Freundlich constants. Sorption coefficients normalized to organic C,  $K_{OC}$ , were calculated by dividing  $K_f$  by the fraction of organic carbon in the sorbents. Hysteresis coefficients,  $H = (1/n_{fd})/(1/n_f)$ , were calculated;  $1/n_f$  and  $1/n_{fd}$  are the Freundlich slopes for the sorption and desorption isotherms, respectively (O'Connor *et al.*, 1980).

#### *DKN successive saturation experiments*

SA-ODA $_{100}$  and SA-HDTMA $_{100}$  organoclays (20 mg) were equilibrated at 20 $\pm$ 2 $^\circ\text{C}$  with 8 mL of 10  $\text{mg L}^{-1}$  DKN solution prepared in CaCl $_2$ . After the suspensions were shaken for 24 h, they were centrifuged and the supernatant liquid removed, analyzed by LSC, and replaced with 8 mL of fresh DKN. This procedure was repeated 14 times. Control and DKN-treated samples were washed, air dried, and analyzed by XRD (Siemens D-500 diffractometer, Siemens, Germany) and FTIR (Nicolet 5 PC spectrometer, Nicolet Instruments Corp., Madison, WI). The XRD patterns were obtained on oriented specimens and FTIR spectra on KBr disks.

## RESULTS AND DISCUSSION

### *Sorbent characteristics*

The larger basal spacings of the organic clays compared with the natural clays, SAz-1-smectite, SWy-2-smectite and SHCa-1, indicated the interlamellar entrance of the alkylammonium in the interlayer (Table 1). The arrangement of the interlayer organic cation in organoclays was determined by the charge of the mineral and the size and amount of the exchanged organic cation (Lagaly, 1982; Jaynes and Boyd, 1991). The basal spacing values suggested that ODA and HDTMA formed paraffin-like complexes in the case of SAz-1 complexes ( $d_{001} > 2.2$  nm), bilayers ( $d_{001} \sim 1.7$ – $1.8$  nm) for SWy-2, and monolayers ( $d_{001} \sim 1.3$ – $1.4$  nm) or bilayers in the case of the SHCa-1. The lower charge of the SWy-2 and SHCa-1 compared to SAz-1, favors the horizontal orientation of the alkyl

chains of the organic cation in the interlayer, which is stabilized by hydrophobic interactions with non-charged regions of the clay surface. The higher charge density of the SAz-1 montmorillonite favors a more vertical arrangement of the alkyl chains giving higher basal spacings (Brixie and Boyd, 1994).

#### *Isoxaflutole kinetic study on natural and organic-exchanged clays*

In a clay-free system, the concentration of isoxaflutole in solution decreased from 0.140 to 0.127 mg L<sup>-1</sup> over a period of 48 h (Figure 2). The 9% decrease in

solution was determined to be the result of hydrolysis to DKN. In the presence of natural clays, the concentration of isoxaflutole in solution also decreased by 9% with SAz-1; by 22% with SWy-2; and by 29% with SHCa-1. No measurable <sup>14</sup>C sorption on the pure clays (SAz-1, SWy-2, and SHCa-1) was observed.

The rate of hydrolysis increased considerably in the presence of organoclays as compared to pure clays. In the presence of organoclays, the concentration of isoxaflutole in solution decreased from 0.140 to ~0.003 mg L<sup>-1</sup> in most cases, with 88% of the initial isoxaflutole hydrolyzed to DKN. The lack of <sup>14</sup>C

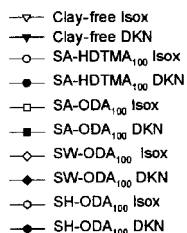
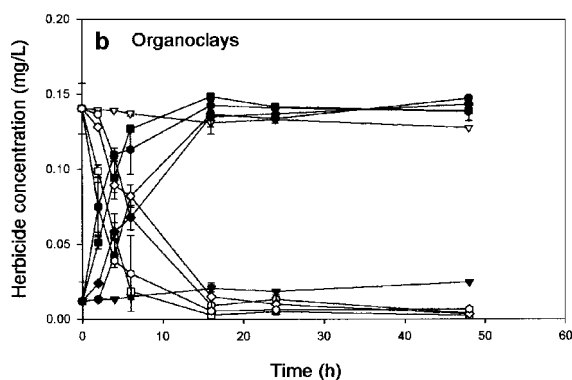
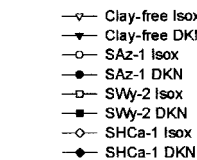
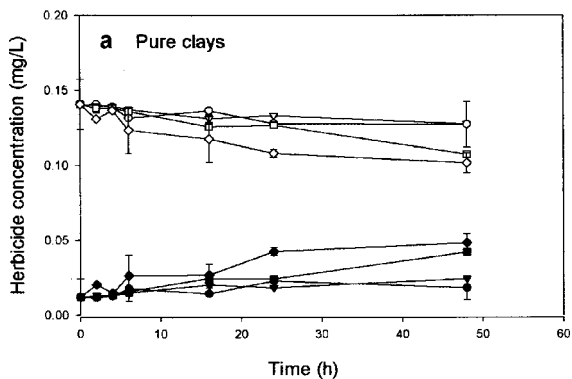


Figure 2. Recoveries of isoxaflutole and diketonitrile over time in clay-free systems, pure clay systems, and organoclay systems. Error bars are standard deviations.

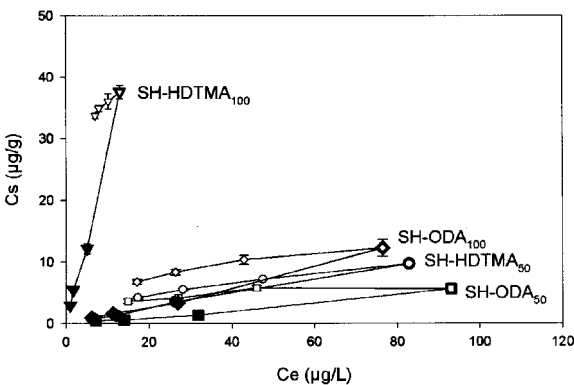
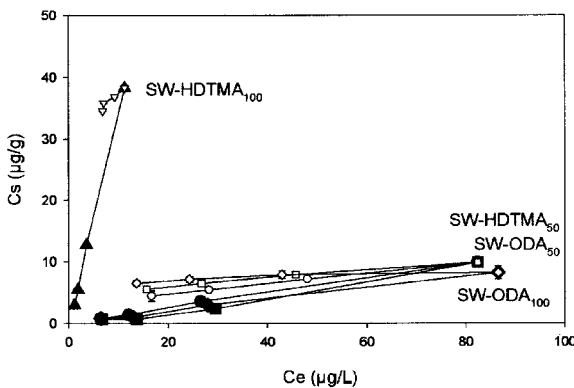
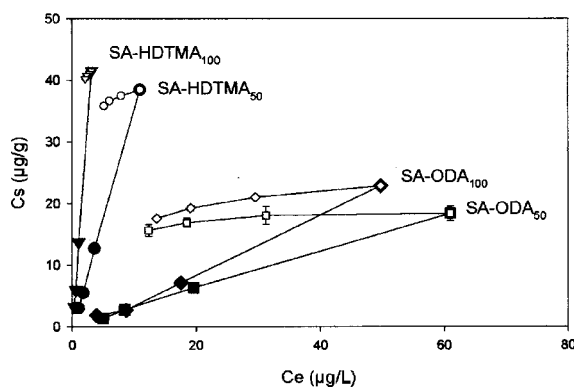


Figure 3. DKN sorption-desorption isotherms on organoclays: solid symbol, sorption; open symbol, desorption. Error bars are standard deviations.

Table 2. DKN sorption-desorption coefficients on natural clays and organoclays.

Sorbent	$r^2$	$K_f$	$1/n_f$	$K_{oc}$	$1/n_{df}$	%H
SAz-1	–	0	–	–	–	–
SWy-2	–	0	–	–	–	–
SHCa-1	–	0	–	–	–	–
SA-HDTMA <sub>50</sub>	0.991	3.16±0.02	1.05±0.03	21	0.09±0.01	9
SA-HDTMA <sub>100</sub>	0.993	12.8±0.03	1.05±0.06	57	0.07±0.01	7
SA-ODA <sub>50</sub>	0.974	0.30±0.06	1.03±0.12	1.2	0.20±0.02	19
SA-ODA <sub>100</sub>	0.996	0.33±0.14	1.01±0.05	1.9	0.10±0.03	10
SW-HDTMA <sub>50</sub>	0.996	0.13±0.06	0.99±0.04	1.3	0.50±0.03	51
SW-HDTMA <sub>100</sub>	0.992	2.7±0.04	1.12±0.07	18	0.17±0.04	15
SW-ODA <sub>50</sub>	0.923	0.06±0.32	1.13±0.23	0.6	0.35±0.01	31
SW-ODA <sub>100</sub>	0.959	0.11±0.19	0.95±0.14	0.7	0.13±0.02	14
SH-HDTMA <sub>50</sub>	0.993	0.12±0.08	1.01±0.06	1.4	0.53±0.01	53
SH-HDTMA <sub>100</sub>	0.990	3.09±0.04	0.94±0.07	23.4	0.17±0.02	18
SH-ODA <sub>50</sub>	0.943	0.06±0.24	0.98±0.17	0.6	0.26±0.09	29
SH-ODA <sub>100</sub>	0.990	0.14±0.09	1.01±0.07	1.1	0.39±0.03	39

Value ± standard error

sorption in the case of the natural clays and minimal hydrolysis, as compared to greater hydrolysis in the presence of organoclays, suggests sorption-catalyzed decomposition. Related to these results, Laird *et al.* (2004) showed that the hydrolysis of triazines in soil environments is catalyzed by acidic sites on the surface of both organic and inorganic constituents. The insecticides diazinon and malathion have also exhibited enhanced hydrolysis in the soil due to sorption catalysis (Armstrong and Konrad, 1974). Hydrolysis of isoxaflutole to DKN in the presence of clays occurred so rapidly that sorption of isoxaflutole could not be characterized. For all the clays, of the actual isoxaflutole remaining, <10% of it was sorbed.

#### Sorption-desorption of DKN on natural and organic clays

The DKN sorption isotherms on organoclays (Figure 3) were fitted to the Freundlich equation (Table 2). No measurable sorption of DKN was observed on the natural clays, SA-smectite, SW-smectite and hectorite. The lack of DKN sorption by the natural clays could be a consequence of the hydrophilic environment at the clay surface and the absence of functional groups on DKN that can interact with the clay surface.

Incorporation of large organic cations in the interlayer of the smectites resulted in organoclays with greater sorptive properties for DKN (Table 2). The isotherms are of C-type (Giles *et al.*, 1960), with  $1/n_f$  values  $\approx 1$  indicating an increase in sorption with an increase in solution concentration. This suggests minimum competition from water molecules for sorption sites, being in agreement with the partition of the chemical through hydrophobic interactions into the interlayer organic phase (Chiou *et al.*, 1983). However, desorption results indicate that partitioning alone may not be responsible for the observed isotherms.

Isotherms in Figure 3 and results in Table 2 show that sorption decreased in the order: SA-HDTMA<sub>100</sub> > SA-

HDTMA<sub>50</sub> > SH-HDTMA<sub>100</sub> > SW-HDTMA<sub>100</sub> >> the rest. It is interesting to note the greater DKN sorption ( $K_f$  and  $K_{oc}$ ) measured on SAz-1 organoclays as compared to the comparable SWy-2 and SHCa-1 organoclays. These data indicate that the vertical arrangement (paraffin-like) of the organic cation in the interlayer provided a better environment for DKN sorption as compared with the horizontal arrangement (bilayer or monolayer) of the alkylammonium in SWy-2 and SHCa-1 (Hermosin and Cornejo, 1992; Jaynes and Vance, 1996).

The nature and amount of the interlayer organic cation play a very important role in the sorption of DKN on organoclays. The results in Table 2 show that HDTMA-saturated organoclays were clearly more sorptive than ODA organoclays, which are less hydrophobic than HDTMA-saturated organoclays. Sorption also increased with the saturation level of alkylammonium in the interlayer. This was confirmed by the  $K_{oc}$  values, which measure the level of efficiency with which alkylammonium adsorbs or interacts with DKN (Jaynes and Boyd, 1991; Hermosin and Cornejo, 1992). These  $K_{oc}$  values indicated that the organic carbon in the fully-exchanged (100% of CEC) HDTMA organoclays was more efficient at sorbing DKN than the organic carbon in the ODA organoclays. For instance, HDTMA organoclays had higher values of  $K_{oc}$  for the organoclays saturated to a greater extent, while low  $K_{oc}$  values and no appreciable differences between low and high saturation were found for the SA-ODA organoclays.

Table 3. DKN sorption of organoclays and initial and final basal spacings ( $d_{001}$ ) values of the organoclays and organoclay-herbicide complexes, respectively.

Sorbent	DKN sorbed (mg g <sup>-1</sup> )	Initial $d_{001}$ (nm)	Final $d_{001}$ (nm)
SA-HDTMA <sub>100</sub>	28	2.3	3.7
SA-ODA <sub>100</sub>	9	3.2	3.2

Table 4. IR absorption bands (in  $\text{cm}^{-1}$ ) of SA-HDTMA<sub>100</sub>, DKN and the SA-HDTMA<sub>100</sub>/DKN complex.

Group vibration	SA-HDTMA <sub>100</sub>	DKN (KBr disk)	SA-HDTMA <sub>100</sub> /DKN complex
$\nu_{\text{OH}}$ free	3623		3628
$\nu_{\text{OH}}$ bonded	3430	3495	3430
		(water in KBr disk)	
$\nu_{\text{CH}}$ aromatic		3083–3032	(overlaped)
$\nu_{\text{CH}}$ aliphatic	2921, 2851	2930	2922, 2851
$\nu_{\text{C}\equiv\text{N}}$ nitrile		2217	2194
$\delta_{\text{HOH}}$	1637		1624
$\nu_{\text{CO}}$		1610–1549	1493
$\delta_{\text{C-H}}$	1469		1466
$\nu_{\text{C}=\text{C}}$		1424	1410
$\nu_{\text{S}=\text{O}}$		1325–1127	1326

After Bellamy (1980), Nakamoto (1997), and references therein

The desorption isotherms, plotted in Figure 3, along with the respective sorption isotherms, show that sorption was largely irreversible ( $1/n_{\text{fd}} < 1/n_{\text{f}}$ , Table 2). This behavior does not agree with the weak hydrophobic interactions of the pesticide molecules within the interlayer organic phase of the organoclays, hence, other types of mechanisms might be involved. Of the quarternary alkylammonium-saturated (HDTMA) clays, sorption was less reversible (lower H values) for the SAz-1 organoclays (even the partially-exchanged (50% of CEC) SA-HDTMA<sub>50</sub>) than for the SWy-2 and SHCa-1 organoclays.

#### Sorption mechanisms

Sorption values of DKN on SA-HDTMA<sub>100</sub> and SA-ODA<sub>100</sub>, estimated after successive treatments of SA-HDTMA<sub>100</sub> and SA-ODA<sub>100</sub> with DKN solution, were 28  $\text{mg g}^{-1}$  and 9  $\text{mg g}^{-1}$ , respectively, which corrobo-

rates the sorption of DKN on organoclays (Table 3). The  $d_{001}$  values at 25°C indicate that the DKN-treated SA-HDTMA<sub>100</sub> expanded from 2.3 nm to 3.7 nm (Table 3) upon sorption of DKN and there was interlayer sorption of DKN in the organoclays (Hermosin and Cornejo, 1993; Cox *et al.*, 1994, 1995). In contrast, there was no change in  $d_{001}$  (3.2 nm) of SA-ODA<sub>100</sub> upon saturation with DKN due to the small amounts of DKN sorbed (Tables 2 and 3) and the large  $d_{001}$  value, which was enough to host DKN without further expansion.

The spectra for SA-HDTMA<sub>100</sub> (Table 4, Figure 4), and SA-ODA<sub>100</sub> (Table 5, Figure 6), show differences in the OH and NH regions, as has been shown in previous work with other pesticides (Carrizosa *et al.*, 2000, 2001). The FTIR band assignments in spectra of SA-HDTMA<sub>100</sub>, SA-ODA<sub>100</sub>, and DKN and their complexes (Figures 4 and 5) were in accordance with Bellamy (1980) and Nakamoto (1997) (Tables 4 and 5).

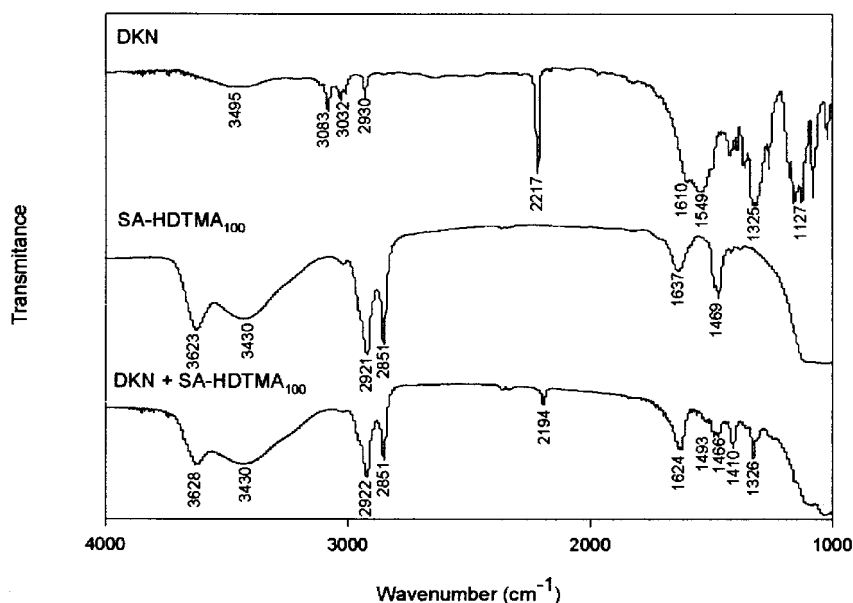


Figure 4. FTIR spectra of: (a) DKN, (b) SA-HDTMA<sub>100</sub> and (c) DKN + SA-HDTMA<sub>100</sub>.

Table 5. IR absorption bands (in  $\text{cm}^{-1}$ ) of SA-ODA<sub>100</sub>, DKN the and SA-ODA<sub>100</sub>/DKN complex.

Group Vibration	SA-ODA <sub>100</sub>	DKN (KBr disk)	SA-ODA <sub>100</sub> /DKN Complex
$\nu_{\text{OH}}$ free	3623	3495	3628
$\nu_{\text{OH}}$ bonded		(water in KBr disk)	
$\nu_{\text{NH}}$ free	3429		3424
$\nu_{\text{NH}}$ bonded	3247, 3180		3250, 3179
$\nu_{\text{CH}}$ aromatic		3083–3032	
$\nu_{\text{CH}}$ aliphatic	2919, 2851	2930	2918, 2850
$\nu_{\text{C}\equiv\text{N}}$ nitrile		2217	2194
$\delta_{\text{NH}}$ free	1636		1635
$\delta_{\text{NH}}$ bonded	1610		1616
$\nu_{\text{CO}}$		1610–1549	
$\delta_{\text{C-H}}$	1470		1469
$\nu_{\text{C=C}}$		1424	
$\nu_{\text{S=O}}$		1325–1127	

After Bellamy (1980), Nakamoto (1997), and references therein

SA-HDTMA<sub>100</sub> shows bands at 3430 and 1637  $\text{cm}^{-1}$  ( $\nu_{\text{OH}}$  and  $\delta_{\text{OH}}$ ) corresponding to molecular water (Figure 4), which do not appear in SA-ODA<sub>100</sub>. SA-ODA<sub>100</sub> shows bands at 3429 and 1636  $\text{cm}^{-1}$  corresponding to the free NH groups of the primary alkylammonium (molecular water can be included in these frequencies), in addition to weak bands at 3247 and 1610  $\text{cm}^{-1}$  arising from NH bonded to basal oxygen atoms of the layer. The different behavior between the organoclays is related to the structure and saturation level of the alkylammonium cations. The long linear chain of the primary alkylammonium may result in a more compact packing of those cations in the interlayer, creating a hydrophobic organic layer, which prevents

water intake. In contrast, the asymmetric structure of the quaternary alkylammonium, as well as its lower saturation level, although also hydrophobic may leave some room between the cations that can be occupied by water molecules, probably associated with basal oxygens of the clay network or to residual inorganic cations.

The DKN molecule has a chemical structure that makes it a suitable probe for an IR study. It is a  $\beta$ -diketone with strongly conjugating attached groups: nitrile, cyclopropyl and phenyl. These groups enhance the formation of the enolic form of the  $\beta$ -diketone, which has acidic character and a proton that could be dissociated (Figure 6). The DKN exists primarily as the enolic form, as deduced by the low frequencies found for

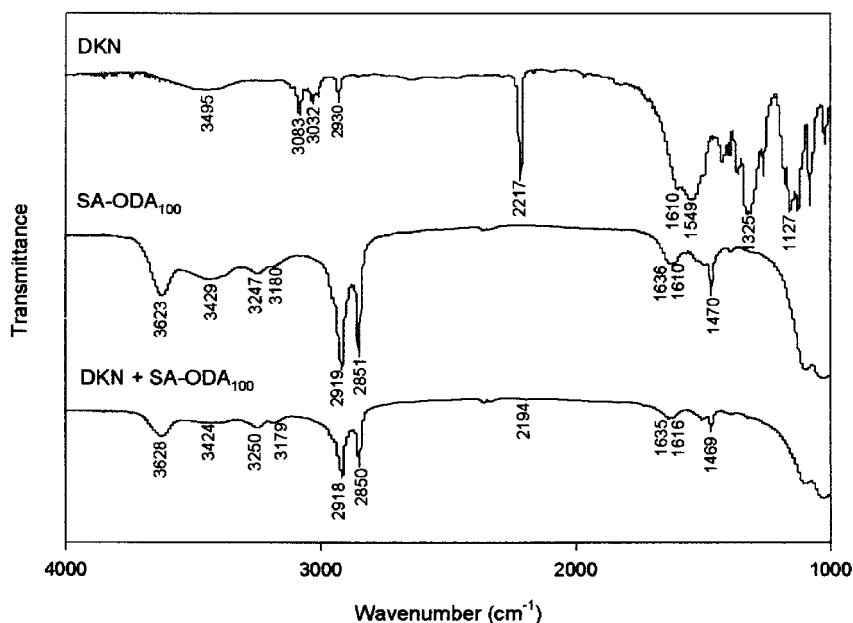


Figure 5. FTIR spectra of: (a) DKN, (b) SA-ODA<sub>100</sub> and (c) DKN + SA-ODA<sub>100</sub>.

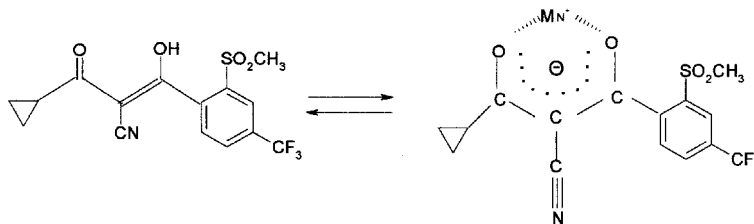


Figure 6. Equilibrium between the enolic form and the chelate.

$\nu_{C\equiv N}$ , 2217  $\text{cm}^{-1}$ , and  $\nu_{C=O}$ , 1610–1549  $\text{cm}^{-1}$ , as compared to those corresponding to the aliphatic nitrile ( $\nu_{C\equiv N}$ ), and ketone carbonyl ( $\nu_{C=O}$ ) at  $\sim 2250$   $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$ , respectively. The conjugation of these multiple bonds through the C=C enolic bond gives support, in addition to the action of the cyclopropyl and phenyl groups, to these low frequencies.

The main feature of the DKN/SA-HDTMA<sub>100</sub> complexes (Table 4, Figure 4) was the shift of the bands corresponding to  $\nu_{C\equiv N}$ , and  $\nu_{C=O}$ , even to lower frequencies, 2194 and 1493  $\text{cm}^{-1}$ , respectively (Tables 4, 5, Figures 4, 5). These extremely low frequencies for  $\nu_{C=O}$  can only be ascribed to the formation of a metallic  $\beta$ -diketonate complex. This species is highly stable due to the stability of the chelate and the resonance effects (Figure 6). Resonance effects decrease the bond order of the carbonyl group and increase conjugation with C $\equiv$ N giving an explanation for the shifting of the frequencies, which are assisted by the cyclopropyl and phenyl groups. In addition, the  $\nu_{C=C}$  of the enolic group decreased from 1424  $\text{cm}^{-1}$  to 1410  $\text{cm}^{-1}$ . The 83% organic cation saturation of this clay implies the presence of residual cations in the interlayer. The formation of stable chelate rings between DKN<sup>-</sup> and the residual interlamellar cations, and/or partially-coordinated structural cations, is in good agreement with the irreversibility observed in the sorption experiments.

In earlier studies, we reported that sorption of some acidic herbicides on SA-HDTMA<sub>100</sub> was mainly due to hydrophobic interactions causing the displacement of water by the herbicide (Carrizosa *et al.*, 2000, 2001). In contrast, water is not displaced by DKN sorption. In this case, strong bands at  $\sim 3430$   $\text{cm}^{-1}$  ( $\nu_{OH}$  bonded) and 1630  $\text{cm}^{-1}$  ( $\delta_{HOH}$ ) remain, as shown in Figure 3. Moreover, the ratio  $\nu_{OH\text{ free}} (\sim 3623 \text{ cm}^{-1})/\nu_{OH\text{ bonded}} (\sim 3430 \text{ cm}^{-1})$  decreased when DKN is sorbed, increasing the bonded OH in relation to free OH. This behavior suggests that basic free OH are protonated in the dissociation of DKN. These protonated groups generate a hydrophilic environment that may prevent water release.

In summary, the FTIR spectra suggest the entrance of DKN into the interlamellar space of the SA-HDTMA<sub>100</sub> and its dissociation in the interlamellar water of the organoclay. The DKN<sup>-</sup> anion then forms a very stable chelate complex with the residual cations and/or

partially-coordinated structural cations. This strong interaction justifies the irreversibility of the sorptive process. No appreciable differences were found between SA-ODA<sub>100</sub>/DKN complex and SA-ODA<sub>100</sub> spectra. A very small band appeared at 2194  $\text{cm}^{-1}$ , corresponding to  $\nu_{C\equiv N}$ . Small variations in the  $\nu_{OH}$  bands and  $\nu_{N-H}$  bands could be related to weak interactions with the solvent. This behavior is in accordance with the very low sorption found for DKN on SA-ODA<sub>100</sub> (Tables 3 and 4).

## CONCLUSIONS

The transformation of isoxaflutole to DKN did not differ significantly between the clay-free system and in the presence of natural clays. Much greater decomposition was found in the presence of organoclays, suggesting sorption-catalyzed decomposition. Modification of natural clays with alkylammonium cations, resulted in organoclays with very high sorptive capacities for the isoxaflutole degradate, DKN. Greater sorption of DKN took place on the paraffin-like organoclays, SAz-1-organoclays, than on the bilayered and monolayered, SWy-2- and SHCa-1-organoclays. Desorption isotherms revealed that sorption of DKN was essentially irreversible. For SA-HDTMA<sub>100</sub>, FTIR spectra suggest the entrance and dissociation of DKN in the interlamellar space of the organoclay. The DKN<sup>-</sup> anion then formed a very stable chelate complex with the residual cations and/or partially-coordinated structural cations. This strong interaction justifies the irreversibility of the sorption process. The enhanced sorption capacity and the irreversible behavior of these organoclays would be desirable in the use of these sorbents for pollutant immobilization in the remediation of contaminated soils.

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