

ADSORPTION MECHANISMS OF IMAZAMETHABENZ-METHYL ON HOMOIONIC MONTMORILLONITE

A. PUSINO,¹ A. GELSOMINO,¹ AND C. GESSA²

¹ Dipartimento di Agrochimica e Agrobiologia, Università di Reggio Calabria
Piazza San Francesco di Sales 4, 89061 Gallina (RC), Italy

² Istituto di Chimica Agraria, Università di Bologna
Via Berti Pichat 11, 40127 Bologna, Italy

Abstract—The adsorption of the herbicide imazamethabenz-methyl, a mixture of the two isomers methyl (\pm)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-4-methylbenzoate (*para* isomer) and methyl (\pm)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methylbenzoate (*meta* isomer), from water onto Al³⁺-, Fe³⁺-, Ca²⁺-, K⁺- and Na⁺-montmorillonite was studied by analytical (HPLC) methods. The adsorption from an organic solvent was also investigated by spectroscopic (IR) and X-ray diffraction measurements. It was observed that, depending on the acidic properties of the exchangeable cations, two different mechanisms may take place. The first one, acting on Fe³⁺- and Al³⁺-clays, involves the protonation of the more basic nitrogen atom of imidazolinone ring of the herbicide because of a proton transfer from the acidic metal-bound water, followed by adsorption on the clay surfaces. In this case, the clay surfaces have greater affinity for the *meta* than the *para* isomer, due to the extra-stabilization of the *meta* protonated form by resonance. The second mechanism, taking place on Ca²⁺-, K⁺- and Na⁺-clays, is hydrogen-bond formation between the ester carbonyl group of the herbicide and hydration water metal ions and is not affected by the structure of the isomers.

Key Words—Adsorption, Hydrolysis, Imazamethabenz-methyl, Infrared spectroscopy, Interlayer cations, Montmorillonite, Pesticides.

INTRODUCTION

The contribution of clay minerals to the adsorption of organic molecules in soil has been the object of several studies (e.g., Mortland 1970, 1976, Pusino *et al* 1991, Laird *et al* 1992, Gilchrist *et al* 1993, Weber 1993). Of the various soil clay constituents, smectites have the greatest potential for adsorption of pesticides due to their large surface area and abundance in agricultural soils (Laird *et al* 1992). Several studies have demonstrated that adsorption mechanisms depend on specific properties such as surface charge density, nature of interlayer cations, and hydration status of the smectites. In most cases, adsorption has been found to promote degradation of pesticides. The extent of such degradation is generally related to the nature of the exchangeable cations (Pusino and Gessa 1990, Sánchez-Camazano and Sánchez-Martin 1991, Pusino *et al* 1993).

Imazamethabenz-methyl, methyl (\pm)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-4-methylbenzoate (*para* isomer) and methyl (\pm)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methylbenzoate (*meta* isomer), is a mixture of *p*- and *m*-methyl 2-imidazolinone toluate. This new herbicide has been developed for control of wild oats (*Avena fatua*) in corn and wheat (Hedlund and Andersson 1987). As it is relatively new, only limited information is available on its herbicidal activity (Brown *et al* 1987, Solntsev *et al* 1990) and its behavior

in the field (Allen and Caseley 1987, Nilsson and Arvidsson 1989). Imazamethabenz-methyl is rapidly photolyzed in solutions and on soils (Curran *et al* 1992) and shows high resistance of the imidazolinone ring toward hydrolysis and oxidation (Rouchaud *et al* 1992). However, interaction studies with soil colloids have not yet been published. The aim of this work was to investigate mechanisms for adsorption of imazamethabenz-methyl on homoionic Al³⁺-, Fe³⁺-, Ca²⁺-, K⁺- and Na⁺-montmorillonite.

EXPERIMENTAL

Materials

Upton, Wyoming, bentonite (No. 25) was purchased from Ward's Natural Science Establishment, Rochester, New York. The <2 μ m fraction was obtained by sedimentation. The cation-exchange capacity (CEC) of the clay (Na form), determined by the BaCl₂ method (Hendershot and Duquette 1986), was 90.2 meq 100 g⁻¹. Al³⁺-, Fe³⁺-, Ca²⁺-, K⁺- and Na⁺-exchanged samples were prepared by immersing the clay into 1 N solutions of the corresponding metal chlorides. The samples were suspended in deionized water and centrifuged at the appropriate speed (12,000–25,000 r.p.m.) and the procedure was repeated several times. When Cl⁻-free, the samples were dried at room temperature. Imazamethabenz-methyl (C₁₆H₂₀N₂O₃), either as *para*- (p-IMZB-M) or *meta*-isomer (m-IMZB-M) (96.2% and 96.8% purity, respectively) or as a 1:1 mixture (m,

p-IMZB-M) (96.4% purity), was supplied by American Cyanamid Co., Princeton, N.J. p-IMZB-M and m-IMZB-M are white solids with a solubility in water of 857 and 1370 mg liter⁻¹ at 25°C, respectively (Wauchope *et al* 1992). Imazamethabenz acid (m, p-IMZB) was prepared by alkaline hydrolysis of m, p-IMZB-M according to the following procedure: 4 ml of 1 N NaOH solution were added to 0.1 g of m, p-IMZB-M. The suspension was stirred at room temperature until clear (about 5 h). After the solution was washed with chloroform, 1 N HCl was added until pH 6 and the acid precipitated. It was filtered and recrystallized from ethanol, giving white crystals. Imazamethabenz-methyl hydrochloride (m, p-IMZB-M·HCl) was prepared by bubbling anhydrous HCl into a chloroform solution of m, p-IMZB-M. The precipitate was filtered and dried *in vacuo*.

Adsorption measurement

Batch distribution isotherms on Al³⁺-, Fe³⁺-, Ca²⁺-, K⁺- and Na⁺-clays were determined at 25 ± 2°C. Duplicate samples of 50 mg of air-dried clay were equilibrated in centrifuge polyallomer tubes with 10 ml of aqueous herbicide solution. To evaluate the adsorption behavior of the two different isomers, isotherms were carried out using solutions containing only the para or meta isomer (range: 10–102 μM) or a 1:1 mixture of them (each with concentration 5–120 μM). The tubes were shaken (end-over-end) for 15 h. Generally, 95% of the adsorption was found to occur within 4 h. After equilibrium was reached, the suspension was centrifuged at 20,000 r.p.m. for 15 min. The supernatant was pipetted off and analysed immediately by high performance liquid chromatography (HPLC). The amount adsorbed by clays was calculated from the difference between the initial and final concentrations of imazamethabenz-methyl in solution. The pH of aqueous suspensions were 3.9, 4.3, 6.2, 6.7, and 7.0 for Fe³⁺-, Al³⁺-, Ca²⁺-, K⁺- and Na⁺-clays, respectively.

The adsorption studies were repeated by immersing air-dried self-supporting bentonite films in ca. 2 vol. % solution of m, p-IMZB-M in CHCl₃. After 24 h the films were separated from the solution and washed with CHCl₃ to remove excess pesticide. After air-drying, the films were examined by infrared (IR) spectroscopy.

Chromatographic analyses

To follow the adsorption from solutions of pure p- or m-isomer, HPLC analyses were carried out using a Waters 510 liquid chromatograph equipped with a 250 × 4 mm i.d. μBondapak® C₁₈ (10 μm) analytical column. A multiwavelength Waters 490 programmable detector operating at 238 nm and a Waters Baseline 810 chromatography work-station were used. The mobile phase (1 ml min⁻¹) was composed of acetonitrile and water (65:35 by volume, pH 3). In these conditions

the retention time of both imazamethabenz-methyl isomers was 4.5 min.

In the case of 1:1 mixtures of the two isomers, HPLC analyses were carried out using a Perkin Elmer LC 250 equipped with a 150 × 3.9 mm i.d. μBondapak® C₁₈ (10 μm) analytical column. A Perkin Elmer LC 135 diode array detector operating at 220 nm (band width 25 nm) and a Perkin Elmer Omega 2 analytical workstation were used. The mobile phase (1 ml min⁻¹) was composed of acetonitrile and water (18:82 by volume). In these conditions the retention time of p- and m-isomer of imazamethabenz-methyl were 22.2 and 24.8 min, respectively.

Physical measurements

Fourier transform infrared spectra (FTIR) were recorded with a FTIR Nicolet 205 spectrophotometer over the range 4000–600 cm⁻¹ (optical resolution, 2 cm⁻¹). IR spectra were obtained in KBr disks except those of clays which were recorded using self-supporting films. Differential spectra were obtained for herbicide-bentonite complexes by subtracting the spectra of the corresponding homoionic clay from those of clay-organic complexes.

XRD data were obtained on a Philips PW 1730 instrument equipped with an Olivetti M-20 computer, using CoK_α radiation, in the 2θ interval 2–17°. Oriented films were prepared by evaporating small volumes of clay suspensions (ca. 2 wt %) on microscope slides. The analyses were carried out at room temperature on the samples which were air-dried or heated at 190°C. The samples were kept in dry atmosphere during the analysis and protected against rehydration by Mylar plastic films.

Data analysis

Adsorption data were fitted by the logarithmic form of the Freundlich equation, $\log c_s = \log K_f + 1/n \log c_e$ where c_s (μmol 100 g⁻¹) is the amount of adsorbed herbicide, c_e (μM) is the equilibrium concentration in solution, and K_f and $1/n$ are empirical constants representing the intercept and the slope of the isotherm, respectively. Because the values of $1/n$ deviate considerable from unity, in some cases it was preferred to use the distribution coefficient $K_d = c_s/c_e$, at the 10 μM level, to measure the adsorption extent.

RESULTS

Adsorption from water

Isotherms for adsorption of m-IMZB-M and p-IMZB-M on homoionic montmorillonites are shown in Figures 1 and 2, respectively. All the isotherms are of "S" type, according to the classification of Giles *et al* (1960). This shape indicates that the adsorption becomes increasingly favored as concentration rises and is usually ascribed to strong competition with the sol-

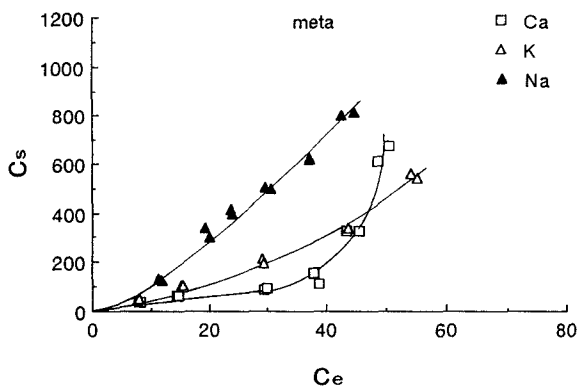


Figure 1. Adsorption isotherms of *m*-IMZB-M on homoionic montmorillonites. C_e ($\mu\text{mole/liter}$); C_s ($\mu\text{mole/100 g}$). Data for Fe^{3+} and Al^{3+} are not shown because of the total adsorption of the molecule over the concentration range investigated.

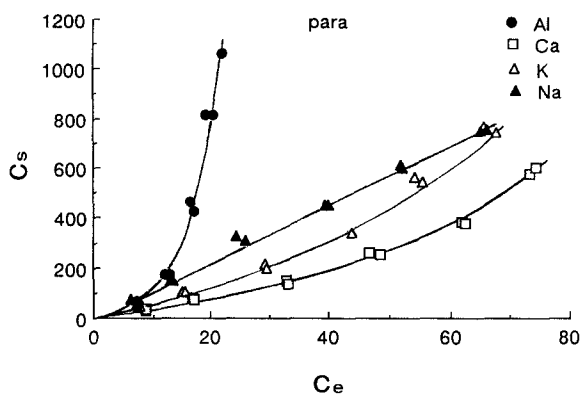


Figure 2. Adsorption isotherms of *p*-IMZB-M on homoionic montmorillonites. C_e ($\mu\text{mole/liter}$); C_s ($\mu\text{mole/100 g}$). Data for Fe^{3+} are not shown because of the total adsorption of the molecule over the concentration range investigated.

vent molecules for substrate sites. In certain instances, especially in the adsorption of organic compounds, the "S" type isotherm is due to cooperative interactions among adsorbed organic species, stabilizing the sorbate and enhancing its affinity for the surface (Sposito 1984). The empirical Freundlich relationship was used to evaluate the results ($r \geq .97$). The values of K_f and $1/n$ are given in Table 1.

The most prominent feature of these results is the different affinity of the homoionic clays for *m*-IMZB-M and *p*-IMZB-M. The Fe-clay samples almost totally adsorbed both the isomers of IMZB-M, whereas, under identical conditions, only *m*-IMZB-M was completely removed by the Al-clay. Because the values of $1/n$ deviated considerably from unity in several samples, it was preferred to assume the distribution coefficient K_d as a measure of the adsorption capacity. Using only K_f to rank the relative adsorption, adsorption on the Ca-, K-, Na-*para* systems would appear to be greater than in the corresponding Al-system (Table 1). However, the greater slope of the Al-system clearly indicates a higher extent of adsorption than in the respective Ca^{2+} -, K^+ - and Na^+ -systems at the highest equilibrium concentrations. This finding suggests that the isotherms

have converged or crossed at low equilibrium concentrations. Instead, both the K_d and K_f values substantiate that no preferential adsorption occurs for the two isomers of imazamethabenz-methyl on Ca^{2+} -, K^+ - and Na^+ -clay. However, the K_f values for the Na- and K-clay are partly affected by a slight degradation of IMZB-ester to IMZB-acid. Actually, under the working conditions reported in the experimental section, a chromatographic peak with a retention time of 3.4 min was found for both isomers and attributed to IMZB free acid by comparison with an authentic sample. This peak accounted for approximately 5 and 11% of the total product distribution on the K- and Na-clay, respectively. Such a behavior suggests that the magnitude of adsorption is influenced by both the nature of the saturating cation and the different chemical structure of two isomers.

On the whole, the results provide clear evidence that i) the overall adsorption of IMZB-M is related to the polarizing power of the clay cation, inasmuch as the Fe- and Al-clays adsorbed much more IMZB-M than Ca^{2+} -, K^+ - and Na^+ -clays; and ii) *m*-IMZB-M has greater affinity for acidic clays than *p*-IMZB-M, especially in the Al-system.

Table 1. Freundlich constants (K_f , $1/n$ and correlation coefficients) and K_d for the adsorption of pure *m*- and *p*-isomer of imazamethabenz-methyl on montmorillonite.

Sample	<i>meta</i>				<i>para</i>			
	K_f	$1/n$	r	K_d^1	K_f	$1/n$	r	K_d^1
Fe^{3+}	2				2			
Al^{3+}	2				0.23	2.73	0.987	105
Ca^{2+}	1.81	1.32	0.974	35	1.99	1.28	0.991	33
K^+	3.88	1.21	0.992	62	3.40	1.26	0.994	63
Na^+	5.82	1.31	0.988	112	5.97	1.07	0.990	101

¹ $c_e = 10 \text{ mM}$.

² Complete adsorption of the molecule was observed over the concentration range investigated.

Table 2. Freundlich constants (K_f , $1/n$ and correlation coefficients) for the adsorption of 1:1 mixtures *m*- and *p*-isomer of imazamethabenz-methyl on montmorillonite.

Sample	<i>meta</i>			<i>para</i>		
	K_f	$1/n$	r	K_f	$1/n$	r
Fe ³⁺	1			543.35	1.29	0.994
Al ³⁺	191.25	2.97	0.968	3.19	2.00	0.987
Ca ²⁺	0.32	1.88	0.968	0.66	1.56	0.970
K ⁺	3.05	1.31	0.990	1.62	1.14	0.994
Na ⁺	3.45	0.99	0.996	2.86	0.92	0.987

¹ Complete adsorption of the molecule was observed over the concentration range investigated.

To check if the simultaneous presence of both the isomers had effect on this trend, isotherms were repeated using 1:1 mixtures of two isomers over a larger concentration range. In all cases, the meta-isomer was adsorbed to a greater extent than the para-isomer (Table 2); this was especially so for the Fe³⁺ and Al³⁺-clays. This difference was less evident on K⁺- and Na⁺-clays. The only exception is represented by the Ca-clay samples, but the deviation is only fictitious, because, once again, the greater slope of the Ca-meta system substantiates a higher adsorption than on the respective Ca-para system at high equilibrium concentrations. The lower adsorption of *m*, *p*-IMZB-M on clays saturated with alkaline and earth alkaline ions, compared with Fe and Al ions, suggests weaker affinity and likely reflects the lower polarizing power of these ions. Moreover, the K- and Na-clays promoted the formation of free acid of herbicide, which was detected by chromatography (see above).

Adsorption from organic solvent

The adsorption of *m*, *p*-IMZB-M on clays was also studied in an organic solvent (CHCl₃). Over the 4000–1000 cm⁻¹ range the FTIR spectra of the two pure isomers were very similar. The only differences were found in the 1000–650 cm⁻¹ region due to the out-of-plane deformation vibrations of the hydrogen atoms on the ring which depend mainly on the positions rather than on the nature of the substituents (Bellamy 1975). Differential spectra are poorly defined in the 1000–650 cm⁻¹ region and not suitable for elucidating adsorption mechanisms. Because of the more close environmental

significance, spectroscopic studies were performed on samples after adsorption of *m*, *p*-IMZB-M rather than pure isomers. Some of the main IR bands of free (*m*, *p*-IMZB-M), protonated (*m*, *p*-IMZB-M·HCl) imazamethabenz and *m*, *p*-IMZB-M clay-complexes are listed in Table 3. The spectra indicate that *m*, *p*-IMZB-M undergoes significant changes upon interaction with montmorillonite surfaces. The spectra of air-dried Fe³⁺- and Al³⁺-complexes, which are very similar to each other and to that of *m*, *p*-IMZB-M·HCl (Figure 3), suggest that *m*, *p*-IMZB-M is protonated at the imidazolic nitrogen atom in the presence of these exchangeable cations. The more acidic water molecules on the clay surfaces are probably the proton source. These samples exhibit different spectra as compared with the corresponding K- and Na-clay complexes, in which the nitrogen atom is not protonated. Neat *m*, *p*-IMZB-M yields an absorption at 1725 cm⁻¹ due to overlap of the stretches of both imidazolinone ring and ester C=O group. Either the adsorption on the Fe- and Al-clay or the treatment with HCl split the overlapped bands into two distinct peaks at 1779–1785 and 1716–1719 cm⁻¹, respectively. The upward displacement is due to an increase of the double-bond character of the C=O group of imidazolinone ring because of electron-withdrawing effects of protonated ring nitrogen. On the other hand, the protonated nitrogen can give rise to hydrogen bonding with the ester C=O group causing a small shift in the frequency (1716–1719 cm⁻¹) as compared with the value of the free molecule (1725 cm⁻¹). Protonation affects also the skeletal vibrations of aromatic ring. These bands, involving carbon-to-carbon stretches, fall in the 1437–1457 cm⁻¹ range for free herbicide and shift to 1493–1519 cm⁻¹ upon protonation. It is interesting to note that the band at 1782 cm⁻¹ denoting protonation of the herbicide is very weak in Ca²⁺-montmorillonite after sorption of *m*, *p*-IMZB-M (Figure 3). Further experiment showed that it is absent in the case of the pure para isomer adsorption. On the other hand, protonation is ruled out by the spectra of K⁺- and Na⁺-clay complexes after adsorption of *m*, *p*-IMZB-M.

The spectra of *m*, *p*-IMZB-M-treated Ca²⁺-, K-, and Na⁺-montmorillonite showed bands at 1704, 1711 and 1720 cm⁻¹, respectively, indicating a perturbation of the ester C=O group by the metal ions through direct

Table 3. Principal infrared absorption frequencies (cm⁻¹) of *m*, *p*-IMZB-M, *m*, *p*-IMZB-M hydrochloride, and air-dried *m*, *p*-IMZB-M-montmorillonite complexes.

Assignment	<i>m,p</i> -IMZB-M	<i>m,p</i> -IMZB-M HCl	Fe	Al	Ca	K	Na
ν_{CO} (lactam ring)	1725	1779	1785	1783	1782 ¹	1720	1720
ν_{CO} (carboxylate)	1725	1719	1716	1716	1704 ²	1711	1720
Skeletal vibration	1457	1493	1518	1519	1456	1455	1452
	1437	1508			1442	1429	1439

¹ Very low.

² Wide.

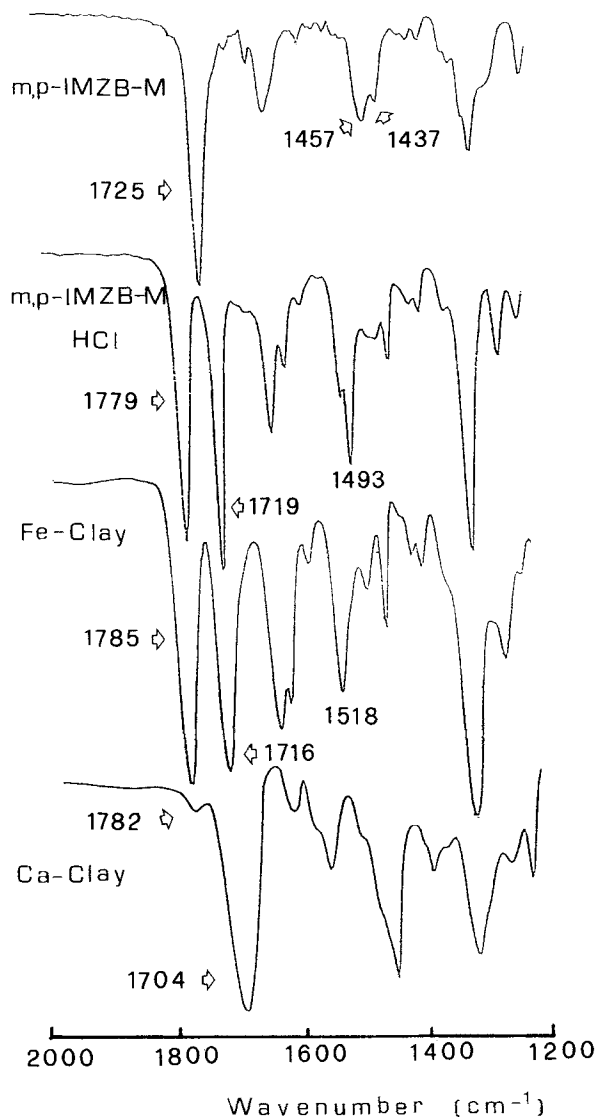


Figure 3. Infrared spectra of *m, p*-IMZB-M (KBr disk), *m, p*-IMZB-M·HCl (KBr disk), and Fe³⁺-, and Ca²⁺-clay treated with *m, p*-IMZB-M. Spectra of clays were recorded as difference spectra with respect to those of untreated samples.

bonds or, more probably, via hydrogen bonding involving water molecules surrounding cations. Such an interaction is expected to lower the force constant of the carbonyl group and decrease the frequency value to a greater extent the higher the polarizing force. A similar behavior was already observed for the adsorption of a number of pesticides on clays (Micera *et al* 1988, Pusino *et al* 1989, Bosetto *et al* 1993).

XRD results

The XRD *d*(001) values (Table 4) of clays before and after treatment with *m, p*-IMZB-M in chloroform solution indicate changes in interlamellar space. In par-

Table 4. *d*(001) values (Å) for homoionic bentonites untreated and treated with *m, p*-IMZB-M¹.

Cation	Untreated		Treated	
	25°C	190°C	25°C	190°C
Fe ³⁺	14.51	9.81	15.39	14.52
Al ³⁺	14.69	10.01	15.50	14.61
Ca ²⁺	14.64	10.62	15.11	11.72
K ⁺	11.61	9.85	12.21	10.52
Na ⁺	12.31	9.64	12.51	10.21

¹ Montmorillonite No. 25 from Upton, Wyoming.

ticular, the magnitude of *d*(001) increased in all samples as an effect of adsorption and the collapse of the interlayer after heating was lower than in the corresponding untreated samples. XRD evidence suggests formation of, at least, monolayer complexes in the Fe³⁺- and Al³⁺-clays. The minor increase of *d*(001) values for the Ca²⁺-, K⁺- and Na⁺-clays could be due to rather random interstratification or low adsorption levels, even if the narrowness of the peaks makes the latter hypothesis more likely.

DISCUSSION

The results of this study demonstrate that the adsorption of imazamethabenz-methyl in the interlayer of smectite clay may occur by at least two mechanisms, both depending on the acidic properties of water molecules coordinated to the exchangeable cations.

The first one, acting on Fe³⁺- and Al³⁺-clays, involves the protonation of the more basic nitrogen atom of the imidazolinone ring of the herbicide because of a proton transfer from the acidic metal-bound water, followed by adsorption on the clay surfaces. A supportive evidence is the similarity between the IR spectra of imazamethabenz-methyl protonated by HCl and those of the Fe³⁺- and Al³⁺-clay complexes. When this mechanism is acting, the clay surfaces exhibit a greater affinity for the meta than the para isomer of the pesticide. According to the mechanism shown in Figure 4, the protonation of imidazolinone ring produces a cation (II) stabilized by resonance because the positive charge can be spread on the benzene ring (III), in particular on the three asterisked carbons. With the meta isomer this cation is rather stable, because of the effectiveness of electron releasing by the methyl group attached to a positively charged carbon. A further canonical form (IV) can be drawn for the protonated meta isomer where there is no bond between carbon and hydrogen, this type of no-bond resonance being called hyperconjugation. None of such stable resonance forms contributes to the structure of the protonated para isomer which, therefore, is less stable than the analogous meta isomer. As a consequence, if adsorption occurs via protonation, para is less favored than meta isomer. Cooperative adsorption and clustering of herbicide

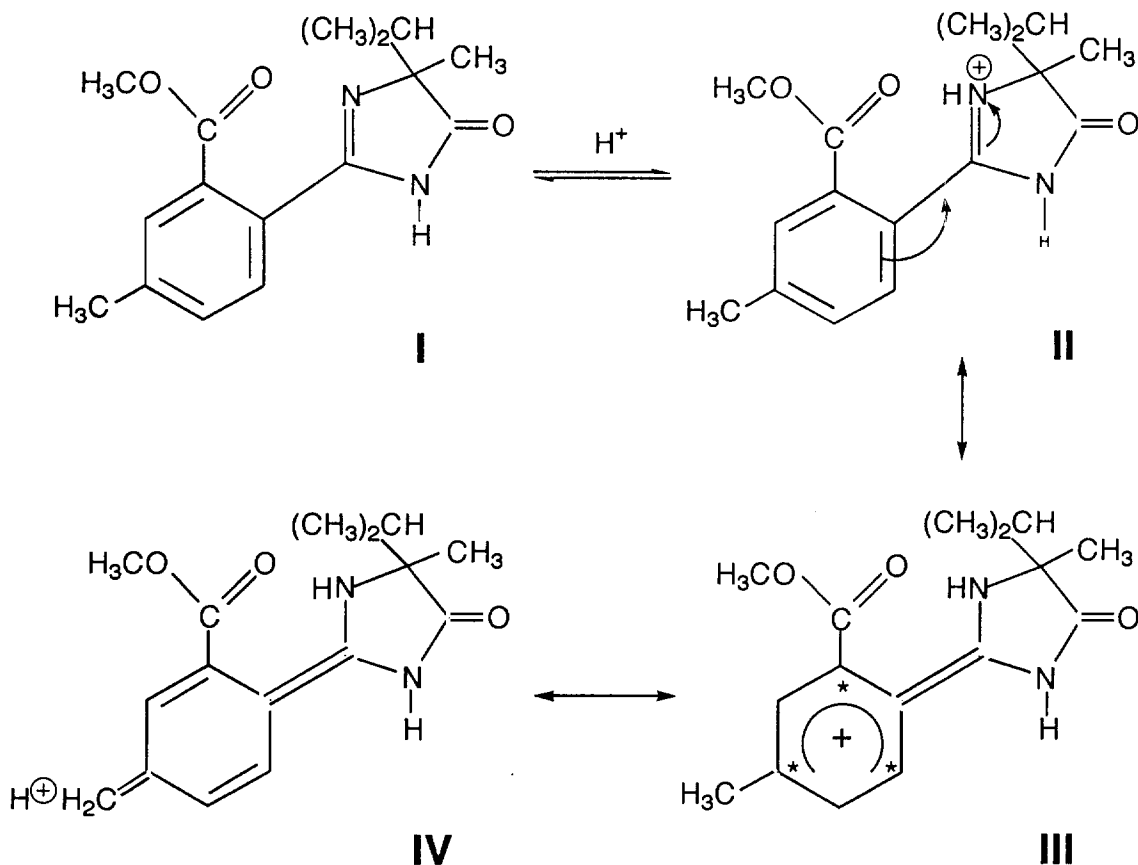


Figure 4. Proposed mechanism for adsorption of m-IMZB-M on Fe^{3+} - and Al^{3+} -clays.

molecules, e.g., due to lipophilic bonds (Hermosin *et al* 1993), may account the "S" type isotherm.

The second mechanism, taking place on Ca^{2+} -, K^{+} - and Na^{+} -clays, is hydrogen-bond formation between the ester carbonyl group of the herbicide and hydration water of metal ions, as substantiated by the shift of $\text{C}=\text{O}$ stretch toward lower frequencies. Such an interaction cannot discriminate between the two isomers of imazamethabenz-methyl ruling out any preferential adsorption. Moreover, this interaction enhances the electrophilic character of the carbonyl carbon and simultaneously weakens the $\text{C}-\text{O}$ bond, facilitating the cleavage of the ester bond by the nucleophilic attack of water. This process affording the free acid as a product is observed on K^{+} - and Na^{+} -clays.

As usual in this kind of studies, correlating spectral and XRD data (often obtained at high loadings, as such for experiments with organic solvent), and adsorption isotherms (measured in water) could be questionable. However, the rather high affinity of the herbicide for the clay leads to high loading levels even in aqueous solution, especially in the presence of Fe^{3+} and Al^{3+} , and this is supportive for a minor role of the solvent and the mutual consistency of the results.

Concerning the acid-base processes involved in the observed mechanisms, both Lewis and Brönsted types of acidity are operating. Actually, the protonation at the nitrogen atom of the pesticide is due to a proton transfer (Brönsted acidity) from water molecules coordinated to the exchangeable cations, but these acidic properties of water are an effect of the Lewis acidity of the cation. Since the clay cation retains in part the bound water molecules even in the presence of chloroform, and these exhibit the most acidic properties, the proton transfer in chloroform is not an unexpected finding.

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