

Protonation–Dissociation Reactions of Imazamethabenz-Methyl and Imazamethabenz-Acid in Relation to Their Soil Sorption and Abiotic Degradation

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This paper presents ultraviolet–visible absorption spectra of imazamethabenz-methyl (IMBM) (mixture of the isomers methyl 6-[(*RS*)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-*m*-toluate, *m*-imazamethabenz, and methyl 2-[(*RS*)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-*p*-toluate, *p*-imazamethabenz) and the corresponding carboxylic acid, imazamethabenz-acid (IMBA). The spectral characteristics are determined as functions of the pH. The appreciable absorbance in the visible (or near-ultraviolet) region of the spectra indicates that the natural photolytic degradation is possible. From variations of the maximum absorbances of the bands, the *pK* values of 3.4 ± 0.2 and 9.4 ± 0.2 were obtained for protonation of the imidazol (=N–) nitrogen and dissociation of the NH imidazol nitrogen of IMBM, respectively. For IMBA, the dissociation *pK* of the carboxylic group is very close to that of the imidazol (=N–) nitrogen, both being close to 3.3. The dissociation *pK* of the NH imidazol nitrogen for IMBA is 9.6 ± 0.2 . The role of the acid–base reactions on the sorption on soils of these herbicides is discussed.

KEYWORDS: Imazamethabenz-methyl; imazamethabenz-acid; *pK*; sorption; dissociation; protonation

INTRODUCTION

Imazamethabenz-methyl (IMBM) is a recently developed imidazolinone herbicide (*I-3*), with its evolution in the environment depending upon the pH of the soil, as for other imidazolinones. Alkaline wet environments permit biological breakdown, and acid dry soils limit their mobility, binding them strongly and making the biological degradation slower. IMBM is a selective systemic herbicide registered for postemergence on wheat (spring and durum) and spring barley. Potential exposure to imazamethabenz-methyl may occur through diet, both food and water, when handling and applying the product or by prematurely entering treated sites. Recently, after a re-evaluation, Health Canada's Pest Management Regulatory Agency is granting continued registration of products containing IMBM for sale and use in Canada (4). Imazamethabenz-acid (IMBA) is a degradation product of IMBM, obtained by hydrolysis that takes place slowly on clays as montmorillonite (5, 6), having herbicide activity itself.

The protonation state of the herbicide is very important in both the sorption on soils and the abiotic degradation of such compounds (5, 6). These two processes depend upon pH through the protonation–dissociation equilibria of the molecules. For IMBM, *pK* values of 2.9–3 (7, 8) and 3.5 (6) have been reported.

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Nevertheless, there is a controversy about the atom involved in this *pK*. Some authors (6) claim that it is due to the protonation of the NH group (imidazol nitrogen) adjacent to the carbonyl arrangement. Acinelli et al. (8) claim that “imazamethabenz-methyl is a weak acid, with a *pK_a* of 2.9, so it is expected to be present in the anionic form at the pH value of the studied soil (8–8.4)”, meaning that they attributed the *pK* to the dissociation of the above-mentioned NH group. Pusino et al. (5) and Tomlin (7) attributed the *pK* to the protonation of another imidazol nitrogen (=N–) present in the molecule. In addition, Brigante et al. obtained only one *pK* for IMBM, but it is known that, for other imidazolinone herbicides, the dissociation of the NH imidazol nitrogen takes place around pH 10–11 (7, 9). As far as the authors know, no studies on the protonation–dissociation equilibria of IMBA have yet been reported.

The first step of IMBM chemical degradation is the saponification of the methoxy group to yield the corresponding benzoic acid, IMBA. Then, other reactions occur to a lesser extent, leading to the opening of the imidazolinone ring (6). This means that the soil pH is a crucial factor in the degradation of IMBM.

Thus, the aim of this work was to obtain the equilibrium constants of the acid–base reactions corresponding to these two imidazolinone compounds by UV spectroscopy to contribute to the knowledge of the effect of the acidity of soils on their sorption and abiotic degradation.

MATERIALS AND METHODS

IMBM (mixture of the isomers methyl 6-[(*RS*)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-*m*-toluate, *m*-imazamethabenz, and methyl 2-[(*RS*)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-*p*-toluate, *p*-imazamethabenz; see **Figure 1**) was kindly supplied by Dr. Chanh T. Ta from BASF Corporation, having quality of analytical standard. IMBA was prepared by alkaline hydrolysis of IMBM as follows (5): 10 mL of 2 M NaOH solution was added to 500 mg of IMBM, and the suspension was stirred at room temperature until clear (about 3 h). The solution was washed with chloroform, and concentrated HCl was added until

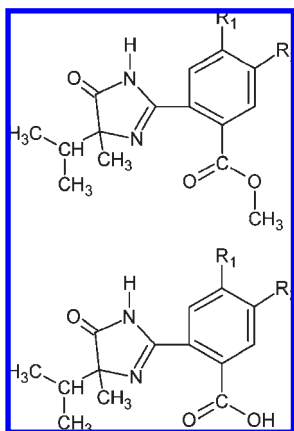


Figure 1. (Top) IMBM and (bottom) IMBA structures. For the *para* isomer, $R_1 = \text{CH}_3$ and $R_2 = \text{H}$, and for the *meta* isomer, $R_1 = \text{H}$ and $R_2 = \text{CH}_3$.

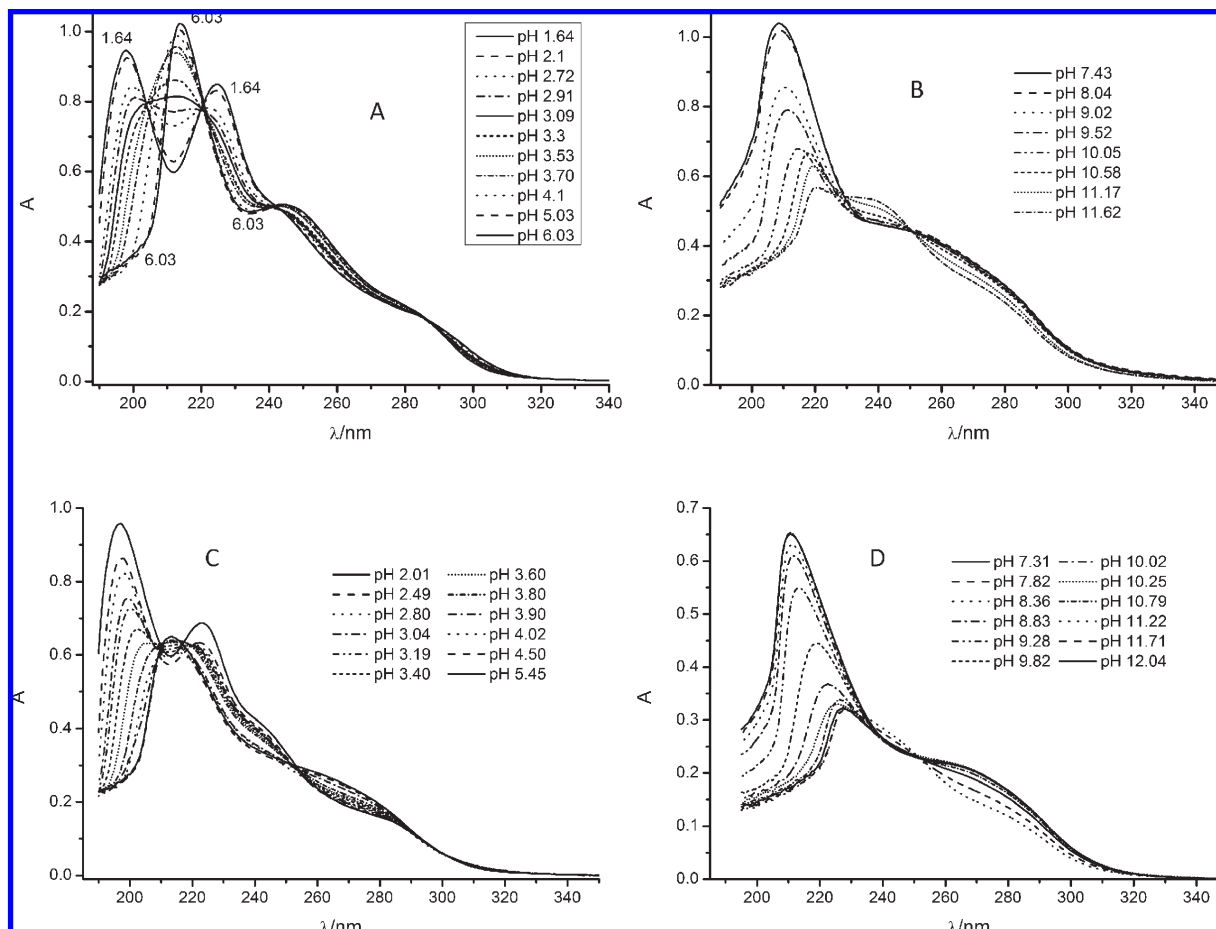


Figure 2. UV-vis spectra of $4 \times 10^{-5} \text{ mol L}^{-1}$ IMBM (A, acidic media; B, basic media) and $4 \times 10^{-5} \text{ mol L}^{-1}$ IMBA (C, acidic media; D, basic media). pH values are given in the legends.

precipitation of the acid that was filtered and recrystallized from ethanol.

Spectrophotometric studies were performed with the following buffers: solutions of perchloric acid at $\text{pH} < 1.5$, 0.1 M phosphoric acid and 0.1 M acetic acid for $1.5 < \text{pH} < 8$, and 0.1 M sodium bicarbonate and 0.1 M phosphoric acid for $\text{pH} > 8.5$. All reagents were of analytical quality and were obtained from Merck. The pH was adjusted with solid NaOH. pH measurements were carried out using a Metrohm pH-meter. Ultra-pure water used was obtained with a Millipore Milli-Q system.

UV-vis absorption spectra (190–390 nm) were recorded with a double-beam Varian Cary 100 Bio spectrophotometer. Hanna quartz cuvettes of 1 cm path length were used.

RESULTS AND DISCUSSION

The absorption spectra as functions of the acidity are shown in **Figure 2** for both IMBM and IMBA. Isobiestic points are observed in both acidic and basic media, indicating that IMBM and IMBA are involved in acid–base equilibria.

The spectral characteristics of IMBM are as follows: at $\text{pH} < 2$, two main bands centered at 198 and 225 nm and two wide shoulders at 245 and 285 nm; at $2 < \text{pH} < 7.5$, one main band centered at 214 nm and two wide shoulders at 245 and 285 nm; at $8 < \text{pH} < 11$, the intensity of the main band decreases with pH and the maximum wavelength changes gradually from 214 to 220 nm, while at the same time, the shoulders shift toward lower wavelength values; and finally, at $\text{pH} > 11$, one main band centered at 220 nm and two wide shoulders at 238 and 275 nm.

In the same way, the spectral characteristics of IMBA are as follows: at $\text{pH} < 2.5$, two main bands centered at 197 and 223 nm

and two wide shoulders at 242 and 281 nm; at $4.5 < \text{pH} < 8$, one main band centered at 213 nm and one very wide shoulder at 266 nm.; at $8.5 < \text{pH} < 11$, the intensity of the main bands decrease with pH, with the band centered at 197 nm disappearing and the wide shoulder gradually splitting into two shoulders at lower and higher wavelengths; and finally, at $\text{pH} > 11$, one main band centered at 223 nm and two wide shoulders at 238 and 274 nm.

In all cases, there is an appreciable absorbance in the visible (or near-ultraviolet) region of the spectra, meaning that the natural photolytic degradation of such compounds by the sunlight absorption is possible (6).

The absorbance was plotted against the pH at a constant wavelength to calculate the equilibrium constant of the acid–base reactions. This is shown in **Figure 3** for IMBM. Sigmoid variations were obtained in both acidic and basic media.

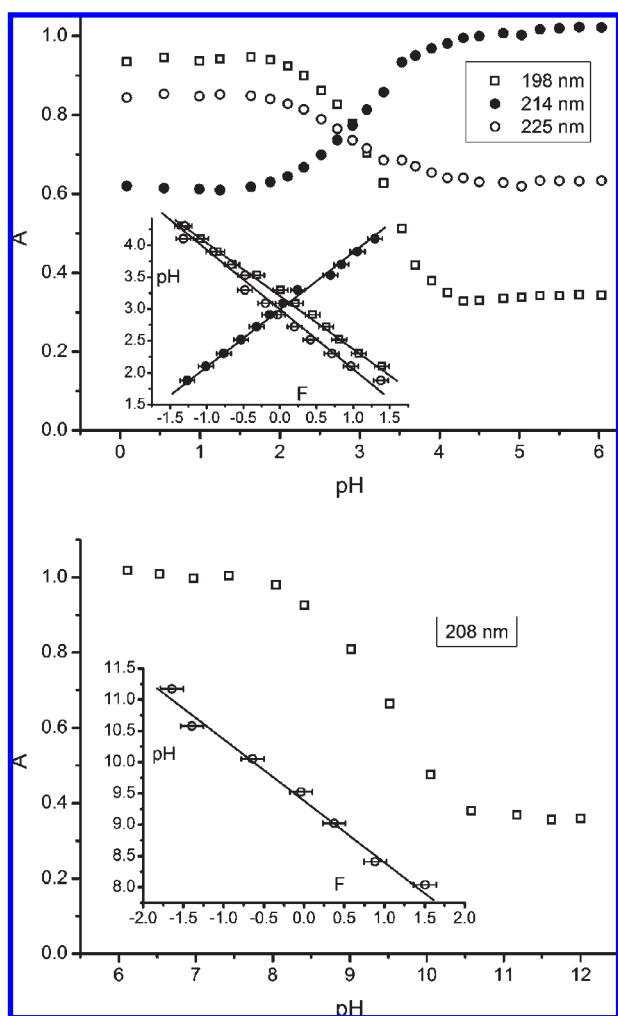


Figure 3. Analysis of UV–vis spectra of IMBM in (top) acidic and (bottom) basic media. (Main graphs) Plots of the absorbance versus pH. Wavelengths are given in the legends. (Insets) Plots corresponding to eq 1.

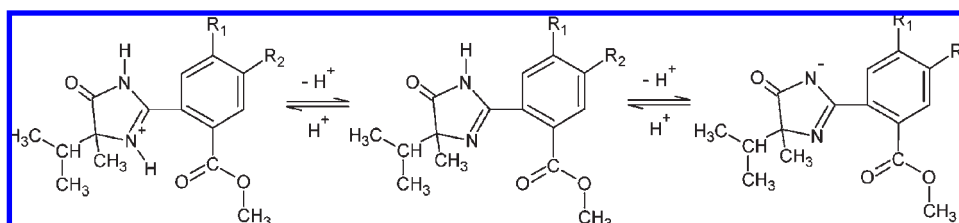


Figure 4. Proposed scheme for the protonation–dissociation reactions of IMBM.

The dependence of the absorbance, A , measured at a constant wavelength versus pH can be expressed as

$$\text{pH} = \text{p}K_a + \log\left(\frac{A - A_0}{A_1 - A}\right) = \text{p}K_a + F \quad (1)$$

where A_0 and A_1 are the constant absorbance values at $\text{pH} \ll \text{p}K_a$ and $\text{pH} \gg \text{p}K_a$, respectively.

From eq 1, it follows that the middle point of the variation must correspond to the $\text{p}K_a$ of the acid–base equilibrium. In addition, the plot of pH versus F must result in a straight line, with a slope close to unity and an intercept of $\text{p}K_a$. This is also shown in **Figure 3** for IMBM.

In all cases, the slopes of the lines are close to unity, and from these plots, values of $\text{p}K_1 = 3.4 \pm 0.2$ and $\text{p}K_2 = 9.4 \pm 0.2$ are obtained for IMBM.

The $\text{p}K_1$ value agrees with those shown in the literature cited in the Introduction. For IMBM, $\text{p}K_1$ can only correspond to the protonation–deprotonation of an imidazol nitrogen that must be the nitrogen ($=\text{N}-$), as for other imidazolinone herbicides (9–11) (**Figure 4**). On the other hand, $\text{p}K_2$ can only correspond to the dissociation of the imidazol nitrogen NH , as found for the rest of imidazolinone herbicides (7, 9).

From the $\text{p}K_1$ and $\text{p}K_2$ values of the acid–base equilibria, it can be inferred that, below pH 3, IMBM is present in a cationic form (IMBMH^+). At the most common pH values found in the environment (5.0–7.5), IMBM is present in the molecular neutral form. Finally, at very basic pH values, IMBM is in an anionic form.

Soil pH is a crucial factor in photodegradation of pesticides on the soil surface, particularly for acid-labile pesticides, such as imidazolinone herbicides (12). Soil moisture is also important because of its role in producing hydroxyl radicals, which in turn cause photodegradation of pesticides (6). Imidazolinones are sorbed through several mechanisms, including ligand exchange, cation and/or water bridging ion exchange, hydrogen bonding, electrostatic interaction, or hydrophobic partitioning (13). Ionization of imidazolinone herbicides increases their solubility in water, resulting in movement in soil. The presence of an anionic form of imazapyr, imazethapyr, and imazaquin at soil pH values greater than the $\text{p}K_a$ causes these herbicides to be repulsed by soil colloids, leading to low sorption at neutral or high soil pH (14, 15). At low soil pH values, imidazolinone herbicides mainly exist as uncharged species that can interact with the hydrophobic surfaces of organic matter and negatively charged soil colloids (16).

In the case of IMBM, ionized forms are present in very acidic and basic media. In the first case, the positive charge must cause the attraction with soil colloids, but such very acidic soils are not common. On the other hand, in basic soils of pH 7.8–8, as used for cereal dry farming in Castilla and Leon, Spain (17), the anionic form of IMBM is present in 4–5%. Although this amount could seem low, the solubility of such an anionic form in water can result in its movement in soil, shifting the dissociation equilibrium to the right to produce the anionic form from the

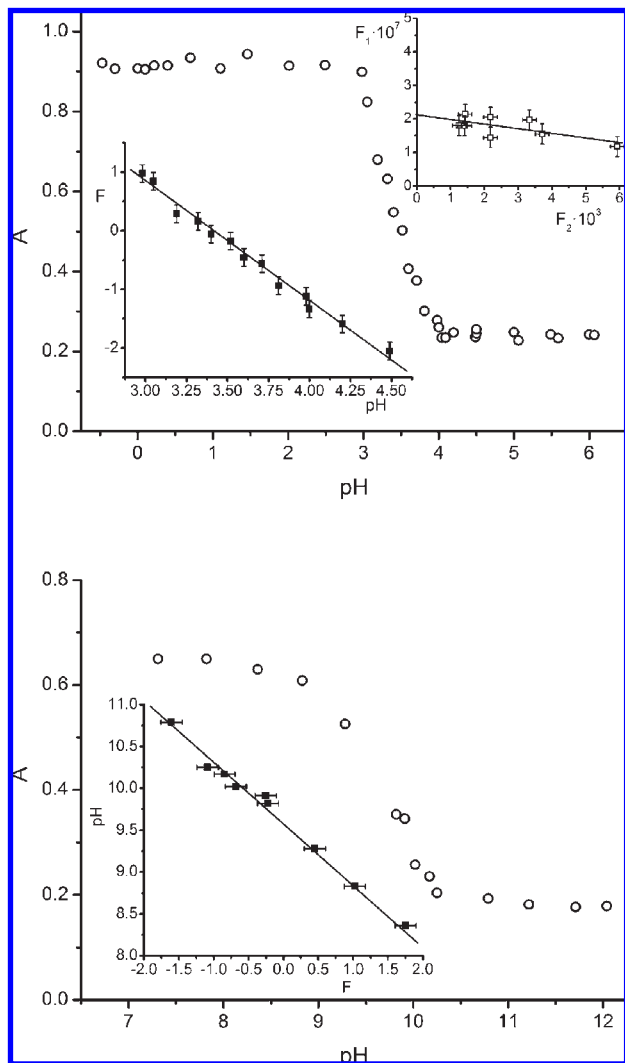


Figure 5. Analysis of UV-vis spectra of IMBA in (top) acidic and (bottom) basic media. (Main graphs) Plots of the absorbance versus pH. Wavelengths are given in the legends. (Insets) (Left) Plots corresponding to eq 1 and (right) plots corresponding to eq 2.

neutral form and, thus, resulting in the movement in soil of IMBM in a greater extension than at lower pH values.

In the case of IMBA, an additional form must be involved in the acid-base behavior because of the presence of the $-\text{COOH}$ group. Thus, in acidic media, the dissociation of the carboxylic group and the protonation of the imidazol nitrogen must originate from the occurrence of two pK values (pK_1 and pK_2) and with the dissociation of the imidazol NH, the apparition of a third pK , pK_3 .

Figure 5 shows the plot of the absorbance measured at a constant wavelength versus pH for IMBA. Again, sigmoidal variations were obtained. In basic media, the plot of pH versus F (eq 1) is linear, having a slope close to unity and, thus, yielding a $pK_3 = 9.6 \pm 0.2$. However, in acidic media, the plot of F versus pH has a slope close to 2 (or the reverse plot close to 0.5), suggesting that two H^+ ions are involved in the reaction. In addition, the range of pH at which the change in absorbance takes place is short. This change occurs in only two pH units, while for a single protonation/dissociation reaction, a change in four pH units is expected. In addition, no other inflection points are obtained, even at very strong acidic media. All of these facts can be easily explained if it is assumed that pK_1 and pK_2 have very close values, of around 3.4.

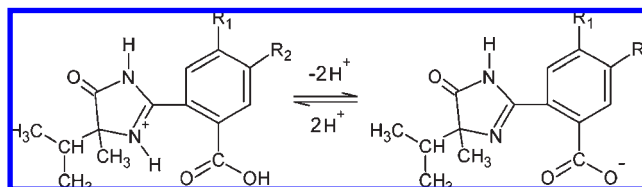


Figure 6. Proposed scheme for the protonation-dissociation reactions of IMBA in acidic media.

The above conclusion can be supported as follows: let us assume that there are three species involved in two subsequent acid-base equilibria. The molar extinction coefficients of such species, ϵ_i , are different, and the acid-base equilibrium constants have similar values, that is, $K_1K_2 \approx K^2$. In such conditions, the following equation is easily obtained:

$$\frac{A - A_0}{A_1 - A} [\text{H}^+]^2 = K^2 + (K - \epsilon c_T) \frac{[\text{H}^+]}{A_1 - A} \quad (2)$$

where the symbols have the above-mentioned meaning, ϵ is the molar extinction coefficient of the intermediate species, and c_T is the sum of concentrations of the three species involved in the equilibria.

The above equation can be written in compact form as

$$F_1 = K^2 + bF_2 \quad (3)$$

Thus, the value of the equilibrium constant can be obtained from the intercept of the linear plot of F_1 versus F_2 , as shown in **Figure 5**. The value of the intercept thus obtained was $2.1 \times 10^{-7} \pm 3 \times 10^{-8}$, with this value yielding $pK_1 \approx pK_2 \approx pK = 3.34 \pm 0.05$.

The above value indicates that, at $\text{pH} < 3.3$, the protonated carboxylic form of IMBA is present and, above $\text{pH} 3.3$, the dominating species is the unprotonated carboxylate form, as shown in **Figure 6**. In addition, the zwitterionic species, either the unprotonated carboxylic form or the protonated carboxylate form, are not present at any pH value, at least in a significant proportion.

Thus, IMBA is negatively charged at $\text{pH} > 3.3$ (the acid-base reaction corresponding to pK_3 adds an additional negative charge), and this must cause this herbicide to be repulsed by soil colloids, leading to a low sorption in soils.

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