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EFFECT OF ZN(II) ON ACID HYDROLYSIS OF METHYLPARATHION

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ABSTRACT

Methylparathion (O,O,-dimethyl O-4 nitrophenylphosphorotioate) kinetic transformation in presence of Zn(II) was studied at pH range from 2 to 7. Between pH 2-5 methylparathion degraded, but at pH 6 and 7 Zn(II) precipitated and the pesticide hydrolysis did not occur. The reaction was first order and the rate constant values were 3.38 x 10^{-2} h^{-1} (pH 2), 7.69 x 10^{-3} h^{-1} (pH 3), 1.31 x 10^{-2} h^{-1} (pH 4) and 1.02 x 10^{-2} h^{-1} (pH 5). Paranitrophenol appeared as the only electroactive product at all pH values. It is proposed that the main degradation pathway for methylparathion in acid medium was a hydrolysis reaction of the pesticide catalyzed by Zn(II), via an electrophilic mechanism.

Palabras clave: metilparatión, Zn(II), hidrólisis, polarografía, paranitrofenol

RESUMEN

Se estudió la cinética de transformación del metilparatión (O,O,-dimetil O-4 nitrofenilfosforotioato) en presencia de Zn(II) en el intervalo de pH de 2 a 7. Se observó la degradación del metilparatión en el intervalo de pH de 2 a 5, sin embargo a pH6 y 7 el Zn(II) precipitó y no ocurrió la hidrólisis del plaguicida. La reacción fue de primer orden y los valores de las constantes de velocidad fueron 3.38 x 10^{-2} h^{-1}, 7.69 x 10^{-3} h^{-1}, 1.31 x 10^{-2} h^{-1} y 1.02 x 10^{-2} h^{-1}, a los valores de pH de 2, 3, 4 y 5, respectivamente. El paranitrofenol fue el único producto electroactivo observado a todos los valores de pH. Se propone que la ruta de degradación principal del metilparatión en medio ácido, fue una reacción de hidrólisis del plaguicida, catalizada por el Zn(II), vía un mecanismo electrofílico.

INTRODUCTION

Methylparathion is an organophosphorus pesticide used commonly worldwide (Sojo *et al.* 1997, Duran-Nah *et al.* 2000, Castaño *et al.* 2003). Most organophosphorus pesticides (OP), including methylparathion, hydrolyze quickly in alkaline solution, but persist under the neutral and slightly acidic conditions, typical of surface waters, soils and aquifer sediments (Lartiges *et al.* 1995, Smolen and Stone 1997). The presence of metal ions, as Zn(II), in acid medium can favor the transformation of these pesticides (Zeinali and Torrents 1998).

According to Smolen and Stone (1997), the divalent metal ion-catalyzed hydrolysis of OP, as methylparathion, can be examined with the three proposed mechanisms: (1) metal ion coordination of the thionate sulfur to enhance the electrophilicity of P; (2) metal ion coordination and induced deprotonation of H_2O to create a reactive nucleophile; and (3) metal ion coordination of the leaving group to facilitate its leaving.

The effect of metal ions on the methylparathion degradation in acid medium, has been evaluated with Hg(II) (Wan *et al.* 1994, Zeinali and Torrents 1998), and Cu(II) (Smolen and Stone 1997, Manzanilla-Cano *et al.* 2001, 2004).

Wan *et al.* (1994) investigated the catalyzed hydrolysis of some OP by Hg(II) ion at pH 5.5. The hydrolysis of methylparathion was found to be first order and the main hydrolysis product was paranitrophenol. Zeinali and Torrents (1998) studied the effect of Hg(II) on the hydrolysis of the methylparathion. The observed rate of hydrolysis was a function of specific mercury species rather than of the total mercury in the solution. Their results suggest that a mix mechanism (electrophilic and nucleophilic) may have to be considered for general metal-promoted hydrolysis of the pesticide.

With regards to Cu(II), Smolen and Stone (1997) concluded that this metal ion yields significant catalysis of the methylparathion, and that phosphorus centered nucleophilic attack by Cu species was the predominant mechanism. Recently, Manzanilla *et al.* (2001, 2004), undertook a study to determine the effect of Cu(II) in degradation of methylparathion in acid medium. Electrochemical characterization of Cu(II) and methylparathion was done in an aqueous medium at a pH range of 2-7. Paranitrophenol appeared as the only electroactive product at all three pH values (2, 4 and 7). The reaction was first order and had rate constants of 10^{-3} h^{-1}.

On the other hand, Zn(II) has not been employed as catalyzer in the degradation of the methylparathion, in acid medium. Only Smolen and Stone (1997) indicate that Zn(II) present a negligible effect on hydrolysis of several OP, including methylparathion, but they do not show experimental data.

In this work, we studied the effect of Zn(II) on degradation of methylparathion, in acid medium, employing the differential pulse polarography (DPP) as detection method, since methylparathion and Zn(II) are electroactive species.

MATERIALS AND METHODS

Equipment

The degradation kinetic was followed using DPP with a Metrohm model 746 VA Processor with a three electrode 747 VA stand system. A dropping mercury electrode was used as the working electrode, Ag° / AgCl (3 M KCl) was the reference electrode and a platinum wire was the auxiliary electrode.

The pH values were determined using a Corning model 350 pH/ion analyzer with a Corning glass combined electrode.

The paranitrophenol and hydrolysis product spectra were obtained with a HP 8452A Diode-Array UV-Visible spectrophotometer, using quartz cells of 1 cm pathway.

Reagents

All chemicals used were of analytical-reagent grade and were used without later purification. Stock solutions were methylparathion (Sigma-Aldrich) 5 x 10^{-3} M in acetone, and zinc (AccuStandard) (1.53 x 10^{-2} M) in water. The buffered pH solution consisted of a mix of boric, orthophosphoric and acetic acid, all at 0.04 M concentration. The same described acid-base substances functioned as supporting electrolyte in the polarographic analysis. Nitrogen 4.8 (Linde, purity 99.9%) was used to eliminate oxygen in the solutions.

Polarogram recording

To produce the polarograms, 20 mL of supporting electrolyte solution adjusted to the desired pH (in the 2-7 range) with NaOH 1.0 M was placed in the electrochemical cell. Nitrogen gas pressure was adjusted to 1 ± 0.2 lb / inch^2 and the solution purged for 20 minutes to eliminate dissolved oxygen. The potential sweep was then done to produce the intensity vs. potential curve (polarogram) for the supporting electrolyte. The potential sweeps were done with a size 4 drop, a 6 mV pulse amplitude, 0.6 s drop permanence time, 16.7 ms measuring time and a 10 mV/s sweep rate.

To produce polarograms for the Zn(II), methylparathion and methylparathion-Zn(II) mixture, Zn(II) and methylparathion solutions were used with a final concentration in the electrochemical cell of 3 x 10^{-5} M. This concentration was suitable to obtain well-defined polarographic signals and monitoring the hydrolysis kinetics.

Potential range

There was displacement towards more negative values in the anodic and cathodic background limits as pH increased. The anodic limit oscillated between 260 and 70 mV with the pH increase (in the 2-7 range) and the cathodic limit was between −1390 and −1820 mV, in the same pH range. Potential measurements were made at the same current value of 1 µA.

RESULTS AND DISCUSSION

Polarographic behavior of methylparathion-Zn(II) mixture

The effect of pH on the two methylparathion signals (i.e. A-MP signal and B-MP signal) and that of Zn(II), in a buffered aqueous medium in a pH 2-7 range are shown in **figure** 1.

The A-MP signal had a symmetrical peak, good resolution and displaced towards more negative potentials as pH increased. The B-MP signal showed no notable variations between pH 2-5, fell significantly at pH 6 and disappeared at pH 7. Its resolution was good at pH 2-4, but at pH ≥ 4 it had potentials very close to the Zn(II) signal, with slight overlap.

The Zn(II) signal had potentials between −1080 and −1123 mV and moved slightly towards more negative potentials as pH increased. It was observed as a well-defined polarographic peak, except at pH 7. No changes in peak intensity due to pH occurred between pH 2 and 5, but this did decrease at pH 6 and 7 due to precipitation of zinc hydroxide. As a result, a Zn(II) blank was measured during the kinetic at pH ≥ 5.

Table I shows the Ep values for the signals involved in the reaction at each pH value.

The chosen experimental conditions established the bases for study of the reaction transformation of methylparathion in the presence of Zn(II) in an aqueous medium at pH 2-7.

Kinetic at pH 2-5

The methylparathion hydrolysis behavior was similar at all pH range 2-5.

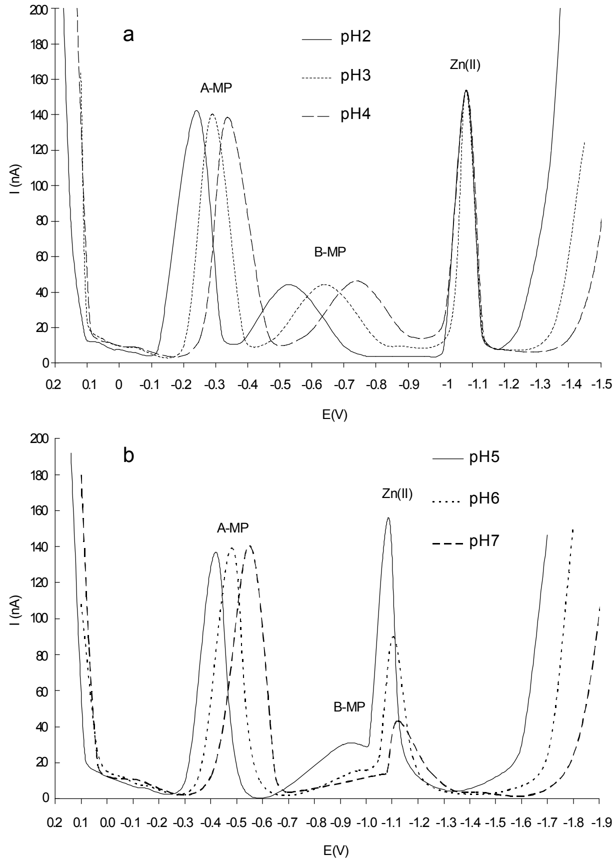

Fig 1. Effect of pH on Ep of A-MP, B-MP and Zn(II) signals: (a) pH range of 2–4, (b) pH range of 5-7

At pH 2, the A-MP and B-MP signals decreased up to 100 hours, at which point they no longer registered on the polarograms. Only the Zn(II) and P1 signals were observed, which were constant after this time period. The P1 signal appeared at 19 hours very close to the A-MP signal and thus may have been masked by it.

At pH 3, the methylparathion concentration decreased, though more slowly than at pH 2. The P1 signal appeared at 48 hours and increased in intensity over time, reaching a maximum at 240 hours. At 96 hours the A-MP signal decreased to half its initial i_p

TABLE I. Ep VALUES FOR A-MP SIGNAL, B-MP SIGNAL, Zn(II) AND PRODUCT 1 (P1) AS A FUNCTION OF pH

	–Ep (mV) vs. Ag°/AgCl					
Signal	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7
A-MP	219	275	330	380	473	548
B-MP	568	610	750	871	-	-
Zn(II)	1082	1084	1082	1088	1105	1119
P1	285	425	410	594	-	-

value and by 264 hours both the A-MP and B-MP signals no longer registered.

Much like at pH 2 and 3, at pH 4 the methylparathion signals exhibited a slow, continuous decrease in intensity. The P1 signal appeared in the polarograms after 20 hours of reaction, then increased until 132 hours after which it remained constant and no MP signals were detected. The Zn(II) had a constant peak current throughout the reaction.

At pH 5, P1 appeared at 26 hours. As pH increased the electrochemical reduction of P1 occurred at more negative potentials and the tendency's uniformity indicated that the electroactive product may be the same at all studied pH values. This reaction was similar to the previous ones in that the B-MP signal disappeared at 94 hours and the A-MP lasted until 166 hours.

Typical kinetic degradation polarograms of methylparathion and their corresponding kinetic curves are shown in **figures** 2 and 3.

Figure 2 shows the polarograms of MP-Zn (II) dissolution at pH 3, at different times. The A-MP and B-MP signals can be seen to decrease as the P1 signal appears, while Zn(II) remains unchanged throughout the reaction. This behavior was similar at all pH values.

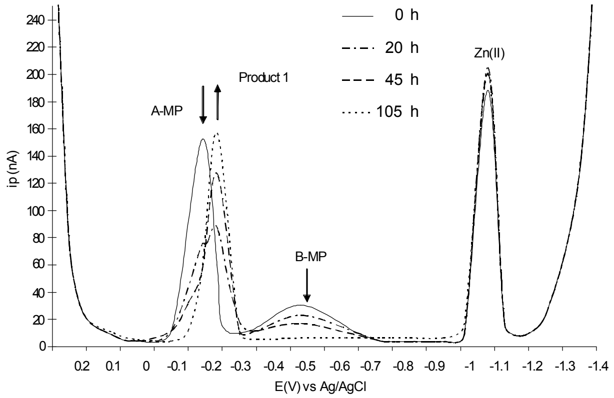

Fig 2. Polarograms showing the MP-Zn(II) mix at pH 3

Figure 3 shows the reaction as a function of reagent and the only electroactive product identified (P1) concentrations, expressed as peak currents of the recorded polarogram signals.

The decrease in the A-MP signal's peak current was seen at all four pH values (2, 3, 4, and 5). This occurred at a determined time at each pH, after which no changes were detected in the signal: at pH 2 this occurred at 100 hours; at pH 3 at 264 hours; at pH 4 at 132 hours; and at pH 5 at 166 hours **(Fig. 4)**. P1 was detected at a different time at each pH value: at pH 2 it was detected at 19 hours; at pH 3 at 48 hours; at pH 4 at 20 hours; and at pH 5 at 26 hours. P1 increased in concentration up to a certain time, which differed for each pH, and then remained constant.

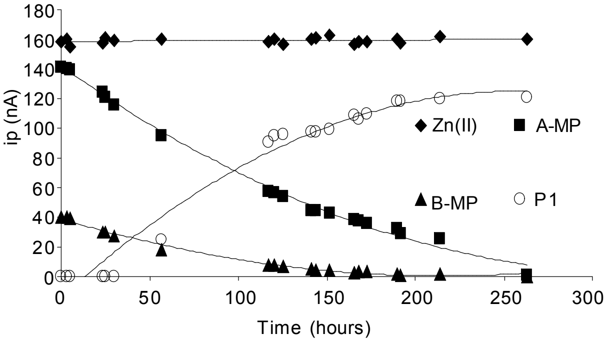

Fig. 3. Transformation kinetic of MP in the presence of Zn(II) at pH 3

Kinetic at pH 6 and 7

Initial intensity of the Zn(II) peak decreased in the experiments done at pH > 5, due to the effect of Zn(II) precipitation as an insoluble metallic hydroxide.

No significant changes were recorded in the A-MP signal over time, meaning that the reaction did not proceed appreciably at these pH values. The Zn(II) peak height decreased up to 100 hours, with a drop of between 40% (pH 6) and 50% (pH 7) relative to its initial current, after which it remained constant. The Zn(II) blank exhibited similar behavior.

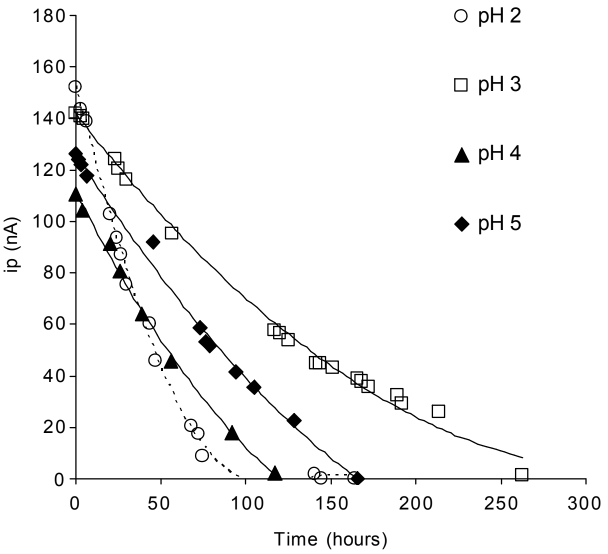

Fig 4. i_p variation vs. t for A-MP signal at pH 2-5

The reaction was monitored for 900 hours, without perceptible changes, indicating that the reaction did not occur in the same way as at lower pH's.

Kinetic parameters

The kinetic study (at pH 2, 3, 4, and 5) experimental results were treated with an integrated method using first, second and third order mathematical models (Manzanilla *et al.* 1997, 2001). Methylparathion concentration was directly proportional to its i_p value, and thus k was calculated as a function of i_p. The experimental data fit the first order model best at all the pH values. **Table II** shows the kinetic parameters from the experimental data between pH 2-5.

TABLE II. KINETIC PARAMETERS OBTAINED FROM THE DEGRADATION OF METHYLPARATHION IN THE PRESENCE OF Zn(II) BETWEEN pH 2 AND 5

pH	Rate constant k (h^{-1}) x 10^2
2	3.38
3	0.77
4	1.31
5	1.02

According to Zeinali and Torrents (1998) and Smolen and Stone (1997), a metal-promoted hydrolysis mechanism dominated by nucleophilic attack by the metal species would show increased rates with increasing pH; a mechanism dominated by the metal acting as an electrophile would show increased rates with decreasing pH.

In this work, Zn(II) presents the characteristic electrophilic behavior, that is to say, the reaction mechanism can be explained by formation of a coordination complex between Zn(II) and the sulphur in methylparathion, which produces an increase in the positive charge density phosphorous, in other words, it becomes more electrophilic. This facilitates the attack on a weaker nucleophile, such as H_2O.

On the other hand, the Cu(II)-promoted hydrolysis presents a mechanism dominated by nucleophilic attack, since, as the concentration of more nucleophilic species increases (pH increase), so does the observed rate for copper (Blanchet and St.-George 1982, Smolen and Stone 1997, Manzanilla *et al.* 2004).

Identification of P1

The potential displacement observed for P1 was similar to that recorded for the A-MP signal at all the studied pH intervals. This similarity in potential values between A-MP and P1 suggests that the structure of the electroactive group of each molecule is similar. In this sense, a known product of basic hydrolysis of methylparathion is paranitrophenol (PNP) which keeps part of the methylparathion structure and thus may be the electroactive product in acid hydrolysis of methylparathion catalyzed by the Zn(II).

To test this hypothesis, the polarograms and UV-Vis spectra for standard PNP were recorded under the same conditions as the reaction study. It was verified that P1 exhibits polarographic behavior similar to standard PNP (**Fig. 5**). The PNP reduction signal moved to a more negative potential as pH increased, which was also noted for P1. To corroborate the assignment of the chemical nature of Product 1, a UV-Vis spectrophotometry study was also done with the reaction mix and the standard PNP solution. The UV-Vis spectra for the reaction mix that contained P1 were compared with those of the standard PNP and it was confirmed that P1 corresponded to PNP at all pH values. Both spectra exhibited the two principal absorption bands of PNP, at 320 nm for the protonated form and 400 nm for the unprotonated form. The 320 band was better defined in both compounds, which is associated with the acid form of PNP.

Figure 6 shows some of the hydrolysis degradation pathways that have been studied for methylparathion. Basic hydrolysis (pH > 7) has been studied previously and requires ^{-}OH ions to occur (Manzanilla

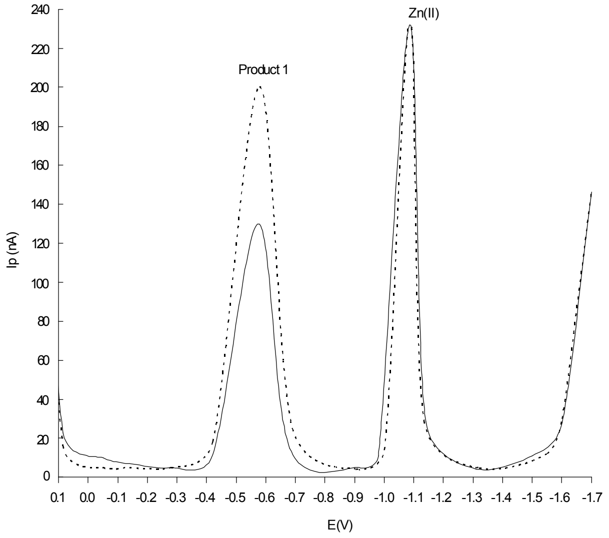

Fig 5. Polarograms of the MP-Zn(II) kinetic at pH 5 (continuous line) and an addition of an aliquot of 60 μL of standard dissolution of paranitrophenol (discontinuous line), at the same dissolution

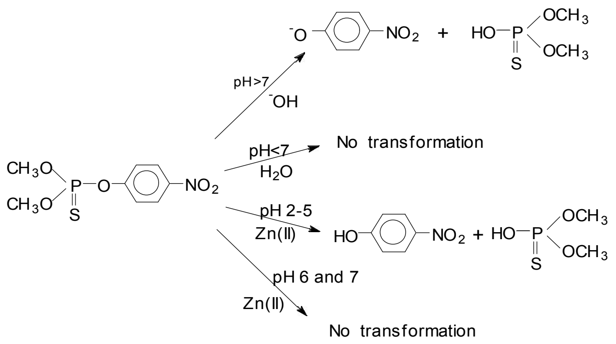

Fig. 6. Methylparathion degradation through basic hydrolysis and acid hydrolysis catalyzed with Zn(II)

et al. 1997). The pesticide's stability in an aqueous medium at neutral or acid pH is also known (pH < 7). The present study suggests the pathways at pH 2-5 in which methylparathion hydrolysis is catalyzed by Zn(II), via an electrophilic mechanism. At pH 6 and 7, however, the pesticide does not degrade in the presence of soluble and precipitated Zn(II) mix.

CONCLUSIONS

The degradation of methylparathion in an acid medium in the presence of Zn(II) was observed in the pH range 2-5. The reaction followed a first order kinetic with rate constant values (k) of $3.38 \times 10^{-2}\ h^{-1}$ (pH 2), $7.69 \times 10^{-3}\ h^{-1}$ (pH 3), $1.31 \times 10^{-2}\ h^{-1}$ (pH 4) and $1.02 \times 10^{-2}\ h^{-1}$ (pH 5).

Differential pulse polarography was shown to be an adequate method for monitoring the reagents and the main product involved in the methylparathion degradation reaction, since most are electroactive, save the dimethylthiophosphate derivative.

Paranitrophenol was identified as a common product, leading to the conclusion that the main degradation route for the pesticide is via Zn(II) catalyzed hydrolysis.

In the probable reaction mechanism, Zn(II) acts as an electrophile in an acid medium.

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