

## Kinetics and mechanism of the degradation of diazinon, malation and chlorpyrifos through silver ion catalytic hydrolysis

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### ABSTRACT

The chemical fate of organophosphorus pesticides is influenced by several factors, one being the chemistry of their aquatic environment. Dissolved metal ions have been shown in several instances to promote the hydrolysis of organophosphorus pesticides, with various reasons forwarded as to the intimate mechanism of metal ion promoted hydrolysis. In this study, we investigate the degradation of diazinon, malation and chlorpyrifos as model for forecast of fate in the presence of metal ions.

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### KEYWORDS

GC;  
Organophosphorus pesticides;  
Metal ions;  
Degradation.

### INTRODUCTION

Organophosphorus pesticides are the most widely used type of chemical for insecticide, herbicide, and fungicide applications. The organophosphorus (OP) pesticides are widely used today in agriculture for field crop protection and fruit tree treatments. Since organophosphorus pesticides are widely used, their fate in the environment is very important.<sup>1</sup> Diazinon (O,O-diethyl-O-[2-isopropyl-6-methylpyrimidinyl]phosphorothioate), is a non-systemic organophosphate insecticide extensively used for pest control. Malathion is a pesticide that is widely used in agriculture, residential landscaping, public recreation areas, and in public health pest control programs such as mosquito eradication.<sup>2</sup> Chlorpyrifos (IUPAC name: *O,O*-diethyl *O*-3,5,6-

trichloropyridin-2-yl phosphorothioate) is a crystalline organophosphate insecticide. The crops with the most intense chlorpyrifos use are cotton, corn, almonds, and fruit trees including oranges, bananas and apples. Pesticide contamination of surface water has been recognized as a major contaminant in world because of their potential toxicity towards human and animals. Under certain conditions, some pesticides may leach to groundwater from normal field applications. Generally, OP degrades in four ways: through hydrolysis,<sup>3</sup> photolysis<sup>4,5</sup>, sonolysis<sup>6</sup>, and microbial degradation.<sup>7</sup> Hydrolysis is one of the most thoroughly studied pathways for the degradation of OP pesticides. Recent research has highlighted the role of metal ions in abiotic degradation processes for the organophosphorus ester and thioester pesticides. The rates of hydrolysis in metal

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ion solutions, such as  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ , were 20-3000 times faster than those of the uncatalyzed reactions. It is postulated that the interaction of metal ions with atoms within  $\text{O} = \text{P}$  or  $\text{S} = \text{P}$  pesticides may enhance their hydrolytic degradation.<sup>4,8</sup> The objective of this research was to investigate the influence of silver ion on degradation of diazinon, malation and chlorpyrifos pesticides.

## EXPERIMENTAL

### Reagents and procedures

Cupric chloride (0.50 M) was prepared by dissolving a weighed quantity of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck) in 5.0 mL of methanol. Silver nitrate (Merck) solution (0.50 M) was prepared by dissolving the weighed amount of  $\text{AgNO}_3$  in 3.5 mL of methanol and 1.5 mL of water. Stock solutions of diazinon, malation and chlorpyrifos prepared (Figure 1.) from Ehrnestorfer (Augsburg, Germany) and the working solutions (0.05 M) were prepared at appropriate concentration in methanol.

In the metal binding studies varying volumes of the substrate and metal stock solutions were then used to obtain metal to pesticide mole ratio of 7.

### Instrumentation

The analysis was performed using a Varian CP-3800 gas chromatograph equipped with a flame ionization detector (FID) and a CP-Sil 8CB (95% polydimethylsiloxane, 5% polyphenyl) fused-silica capillary column (25 m  $\times$  0.32 mm i.d. and 1.2  $\mu\text{m}$  film thickness, Varian, USA). The injector and detector temperatures were 250  $^\circ\text{C}$ , 250  $^\circ\text{C}$  of the sample was injected with a CP-8400 autosampler in the splitless mode. A constant flow (0.9  $\text{mL min}^{-1}$ ) of helium (99.999% purity, Roham Gas Company, Tehran, Iran) was used as carrier gas. The temperature program used for the chromatographic separa-

tion was as follows: 45  $^\circ\text{C}$  for 2 min, temperature increase at 25  $^\circ\text{C min}^{-1}$  to 100  $^\circ\text{C}$  and hold for 2 min, and then temperature increase at 5  $^\circ\text{C min}^{-1}$  to 280  $^\circ\text{C}$ , where it was finally held for 2 min. Hydrogen gas was generated by a hydrogen generator (SCHMIDLIN, USA) at a flow rate of 30  $\text{mL min}^{-1}$ , the flow rate of zero air (99.999%, Air Products, UK) was 300  $\text{mL min}^{-1}$  and the flow rate of makeup (nitrogen) was 25  $\text{mL min}^{-1}$  for FID. A Varian Workstation 5 software was used for data collection and processing.

## RESULTS AND DISCUSSION

Some primary experiments were done for investigation of effect of silver and copper ions on OPPs degradation. The results show opps was degraded completely in the present of silver ions at 10:1 metal ions to pesticide mole ratio, and the copper ions cannot solvolysis pesticides in one hour. Thus, silver ions were selected for investigation of kinetic of pesticide degradation.

### Diazinon, malation and chlorpyrifos degradation in the presence of $\text{Ag}^+$ ions

Diazinon, malation and chlorpyrifos degradation in the presence of  $\text{Ag}^+$  was studied at metal ion/pesticide mole ratios of 1, 2, 3, 4, and 7, separately. The best results obtained in metal ion/pesticide mole ratios of 7.0. For kinetic investigation 0.5 mL of solution containing diazinon (0.7  $\text{mol L}^{-1}$ ), malathion (1.0  $\text{mol L}^{-1}$ ) and chlorpyrifos (1.1  $\text{mol L}^{-1}$ ) was mixed with 0.5 mL of 0.0167  $\text{mol L}^{-1}$  silver nitrate and at times of 0, 38, 76, 114, 152, 190, and 228 min, 1.0 microlitr of solution injected to GC-FID. The degradation of OPPs over time in the presence of  $\text{Ag}^+$  was monitored using GC-FID. As shown in Figure 2, diazinon, malation and chlorpyrifos degraded with increasing of time. The silver ion is

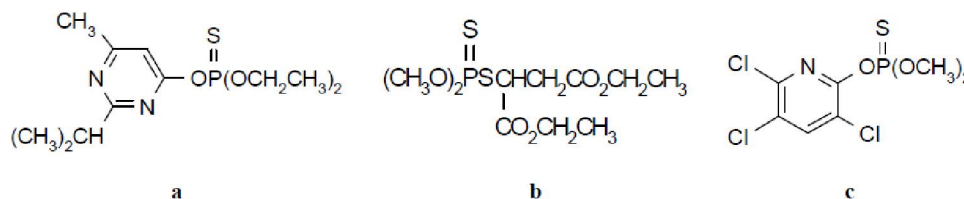
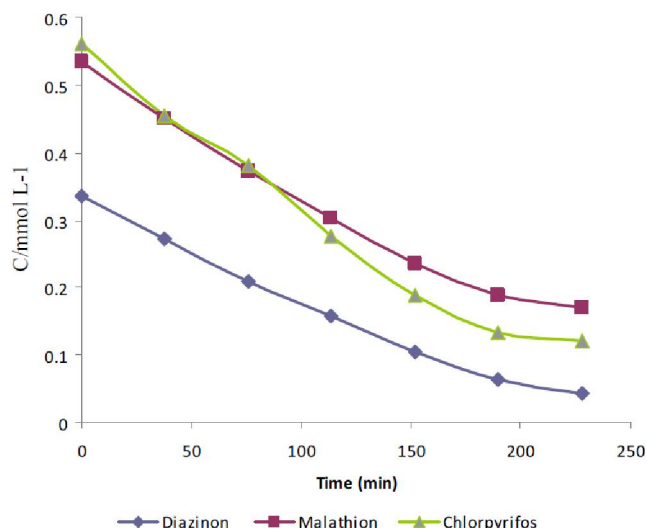


Figure 1 : Chemical structure of OPPs studied in this work. a) Diazinon, b) malathion c) chlorpyrifos

**TABLE 1 : Retention time of GC and observed degradation product diazinon, malation and chlorpyrifos in the presents of  $\text{Cu}^{+2}$  and  $\text{Ag}^+$  ions**

ion/pesticide mole ratio	Ag <sup>+</sup>			Cu <sup>2+</sup>		
	Retention time (min)			Retention time (min)		
	Diazinon	Malathion	Chlorpyrifos	Diazinon	Malathion	Chlorpyrifos
	26.0	29.2	29.5	26.0	29.2	29.5
1	Partially hydrolyzed	Partially hydrolyzed	Partially hydrolyzed	Partially hydrolyzed	Partially hydrolyzed	Partially hydrolyzed
10	Completely hydrolyzed	Completely hydrolyzed	Completely hydrolyzed	Partially hydrolyzed	Partially hydrolyzed	Partially hydrolyzed



**Figure 2 : Concentration profile of selected OPP (0.00125 mol L<sup>-1</sup>) in the present of Ag<sup>+</sup> (0.0083 mol L<sup>-1</sup>) versus time**

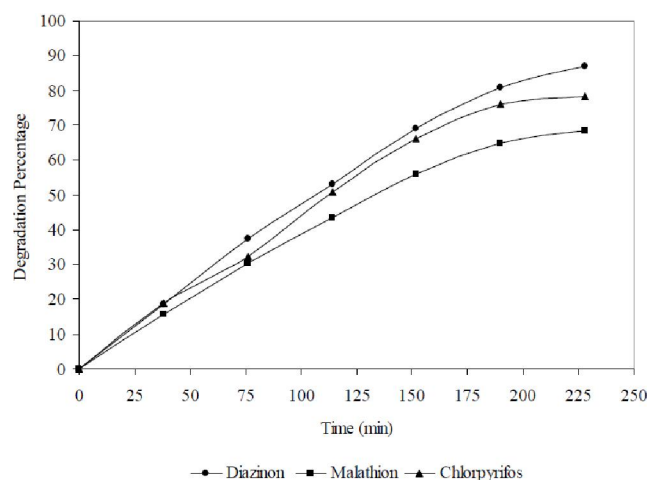
bound to the sulfur atom tightly as expected by Pearson's hard and soft acid-base (HSAB) theory.

The definition of OPP degradation percentage (DP) was as follows:

$$DP = (C_1 - C_2) / C_1 \times 100$$

Where DP (%) is the degradation percentage of the pesticide,  $C_1$  is the initial concentration of OPP (mol L<sup>-1</sup>),  $C_2$  is the concentration of OPP (mol L<sup>-1</sup>) after reaction for (t) time. As you can see from Figure 3, degradation percentage for selected pesticides is higher than 70% after 3 hour.

If a reaction rate depends on a single reactant and the value of the exponent is one, then the reaction is said to be first order and the concentration of a reactant remains constant (because it is a catalyst or it is in great excess with respect to the other reactants), its concentration can be included in the rate constant, obtaining a pseudo-first-order (or occasionally pseudo-second-order) rate equation.



**Figure 3 : Pesticide degradation percentage of selected OPPs (0.00125 mol L<sup>-1</sup>) in the present of Ag<sup>+</sup> (0.0083 mol L<sup>-1</sup>) versus time**

The rate law for an elementary reaction that is first order with respect to a reactant A is:

$$C_t = C_0 e^{-kt}$$

Where  $C_t$  represents the concentration of the chemical of interest at a particular time, and  $C_0$  represents the initial concentration and  $k$  is the first order rate constant, which has units of time<sup>-1</sup>. The integrated first-order rate law is:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt$$

A plot of  $\ln\left(\frac{C_t}{C_0}\right)$  vs. time  $t$  gives a straight line with a slope of  $-k$  with coefficient of regression better than 0.98. The half-life of a reaction describes the time needed for half of the reactant to be depleted (same as the half-life involved in nuclear decay). The half life of a first-order reaction is independent of the starting concentration and is given

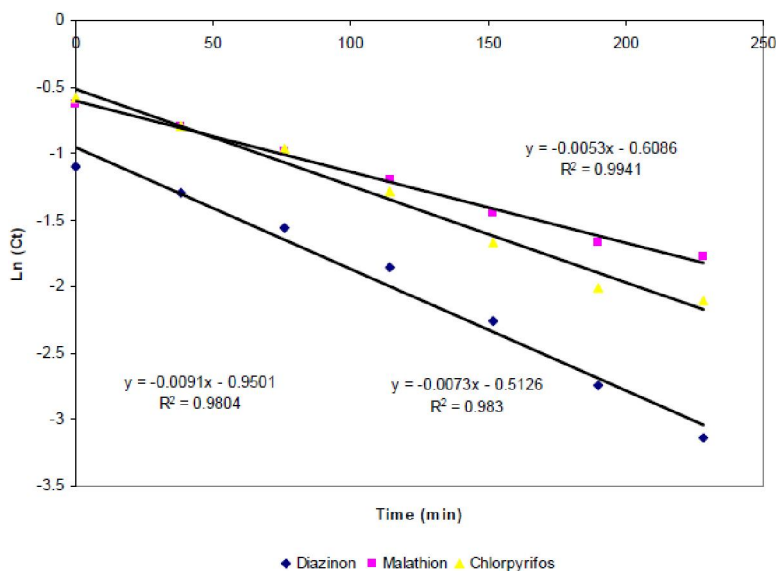


Figure 4 : Plot  $\text{Ln}\left(\frac{C_t}{C_0}\right)$  of versus time for selected OPPs

TABLE 2 : First-order reaction degradation rate constant and correlation coefficient of chlorpyrifos and phoxim (conditions: 0.05 mol L<sup>-1</sup> of chlorpyrifos)

Pesticide	Ag+/ Pesticide	Kinetic equation	$k$ (min <sup>-1</sup> )	$t_{1/2}$ (min)	$R^2$
Diazinon	7	$\text{Ln}(C_t) = -0.0091t - 0.9501$	0.0091	76	0.9804
Chlorpyrifos	7	$\text{Ln}(C_t) = -0.0073t - 0.5126$	0.0073	95	0.983
Malathion	7	$\text{Ln}(C_t) = -0.0053t - 0.6086$	0.0053	131	0.9941

by:

$$t_{\frac{1}{2}} = \frac{\text{Ln}(2)}{k}$$

The reaction rate of is as follow: diazinon > chlorpyrifos > malathion (Figure 4. And TABLE 2). It may be related to chemical structure of pesticides: pesticides with pyridine substitution has higher rate. In the presence of metal ions because of the feasible nucleophilic attacking to the electron deficient phosphorus atom as silver ion bind to the adjacent sulfur atom.

## CONCLUSION

Our results provided direct experimental for enhanced hydrolysis rates of organophosphorus pesticides in the presence of silver ions because of the feasible nucleophilic attacking to the electrondeficient phosphorus atom by complexation of silver ion to the adjacent sulfur atom.

## REFERENCES

- [1] D.D.Richardson, A.J.Caruso; *Anal.Bioanal.Chem.*, **389**, 679 (2007).
- [2] M.Shayeghi1, M.H.Dehghani, A.H.Mahvi, K.Azam, *Iran J.Arthropod-Borne Dis.*, **4(2)**, 11 (2010).
- [3] H.Modra, D.Vrskova, S.Macova, J.Kohoutkova, J.Hajslova, I.Haluzova, Z.Svobodova; *Bull Environ Contam Toxicol.*, **86**, 601 (2011).
- [4] H.Choi, K.Yang, J.Keun Park, I.S.Koo; *Bull Korean Chem.Soc.*, **31**, 5 (2010).
- [5] S.Navarro, J.Fenoll, N.Vela, E.Ruiz, G.Navarro; *J.Hazardous Materials*, **172**, 172, 1303 (2009).
- [6] F.Benoit-Marqui, C.De Montety, V.Gilard, R.Martino, M.T.Maurette, M.Malet-Martino; *Environ.Chem.Lett.*, **2**, 93 (2004).
- [7] J.Lipok, T.Owskiak, P.Mlynarz, G.Forlani, P.Kafarski; *Enzyme Microb.Tech.*, **41**, 286 (2007).
- [8] I.S.Koo, D.Ali, K.Yang, G.W.VanLoon, E.Buncel; *Bull Korean Chem.Soc.*, **30**, 6 (2009).