

On the Mechanism of Dichlorvos Hydrolysis

TATIANA ONCESCU* PETRUȚA OANCEA

Department of Physiscal Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blvd.,30018, Bucharest, Romania

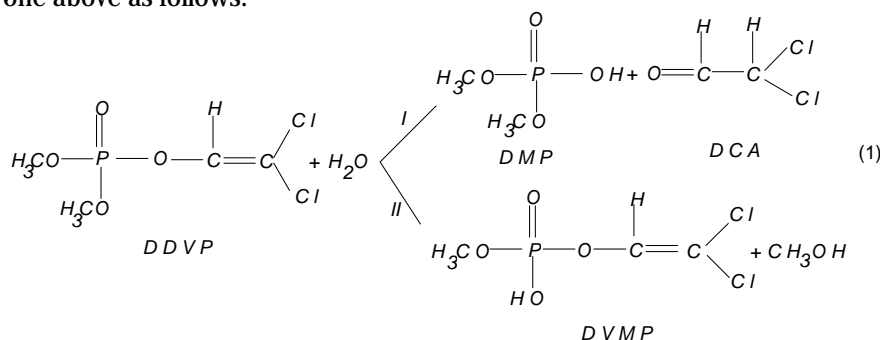
The hydrolysis of Dichlorvos (DDVP) in aqueous solutions of different pH_0 resulting from H_2SO_4 or $NaOH$ addition was studied. Our experiments demonstrated that the acid-catalyzed reaction of dichloroacetaldehyde (DCA), one of the hydrolysis products, superposed on the base-catalyzed DDVP hydrolysis. The presence of Cl^- ions measured in solutions supports this assumption. The bond order calculations of the parent DDVP molecule, as well as of dichlorovinylmethyl phosphoric acid (DVMP) and of dimethyl phosphoric acid (DMP), its hydrolysis products, offer a theoretical agreement with the hydrolysis mechanism. The absence of PO_4^{3-} in solution suggests that monomethyl phosphoric acid (MMP), is the final reaction product. A pseudo first order kinetic was determined for DDVP hydrolysis, and the total rate constant k_t was calculated for each sample with different initial pH . An optimum was found at pH 6 regarding the variation of ΔpH , ΔE and k_t with the initial solution pH value according to the suggested mechanism.

Keywords: dichlorvos, pesticides, hydrolysis, bond order

It is known that the organophosphate pesticides may retain their toxicity for a longer period than expected after application. As a consequence, they are more hazardous than commonly supposed [1].

Dichlorvos – 2,2 dichlorovinyl phosphate (DDVP), is a toxic pesticide which contaminates the surface and even the ground water. It is unstable in water with formation of the highly reactive dichloroacetaldehyde (DCA), and dimethylphosphoric acid (DMP). The phosphorus atom is electron deficient, and nucleophilic attack is the first step in the hydrolytic reaction[2]. Khandlwal and Wedzicha[3] consider that hydrolysis is a base-catalyzed cleavage of the phosphate-dichlorovinyl bond, DCA being liberated in its enol form. One can conclude that the hydrolysis of DDVP may occur by a homogeneous mechanism where H_2O and OH^- act as nucleophiles in an S_N2 mechanism[4].

In order to reduce the environmental risk, its degradation was studied by many authors, but generally they carried out their experiments at $pH \leq 4$ to prevent hydrolysis[5,6]. Mazierski[7] studied the kinetic of DDVP hydrolysis in various buffers of different pH . He demonstrates that this hydrolysis is a general base-catalyzed reaction and proposed also a second route which parallels the one above as follows:



But Mazierski did not analyze any hydrolysis products. The literature being scarce on this subject, we decided to reinvestigate DDVP hydrolysis in order to bring new theoretical and experimental supports for its reaction mechanism.

Experimental part

Material

We used the following substances in our experiments: -dichlorvos (DDVP) Riedel de Haen, 98% purity with a density of 1.412. This value permitted us to calculate the volume (mL) which had to add in a calibrated flask of water in order to prepare the solution of DDVP, in a certain concentration (in our case $1.6 \times 10^{-4} M$).

H_2SO_4 (Merk) and $NaOH$ (Chemapol) p.a. were used to obtain the pH s between 4-6 and 6-10, respectively, of the initial solution.

-Chromotropic acid (Sigma) p.a. was used for the detection of methanol.

-Malachite green (Chemapol) p.a. was used as the color reagent for PO_4^{3-} determination[8], by measuring the absorbances at $\lambda = 660$ nm. Of course, previously it was necessary to establish a calibration curve.

Methods

-The absorbtion spectrum of DDVP samples as well as the absorbance measurements for PO_4^{3-} determination were carried out with an Unicam α -Helios spectrophotometer.

-For the determination of Cl^- concentration, we used a sensor electrode (ISE25Cl-9) delivered by Radiometer accuracy ± 1 mV. Previously, it was calibrated with KCl for each initial pH of the investigated solutions.

- pH was measured with a digital Radiometer pH -meter, beforehand calibrated with the three buffers for pH 4, pH 7 and pH 10 delivered by Radiometer, accuracy ± 0.01 .

* email: poancea@gw-chimie.math.unibuc.ro

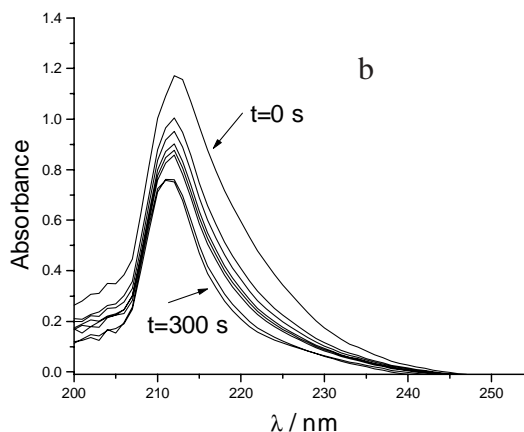
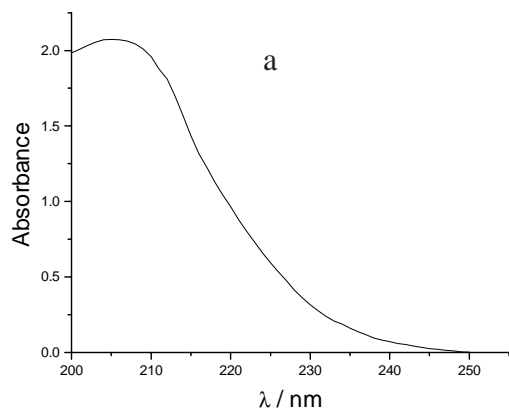
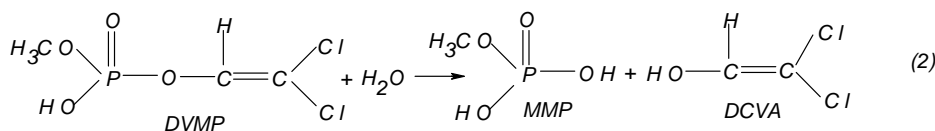


Fig.1. DDVP absorption spectrum: a) pH4, b) pH10

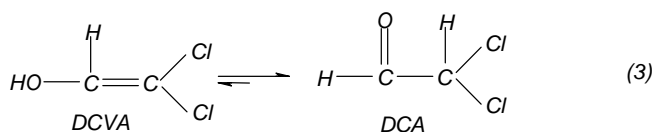
Results and Discussion

Our experiments showed that whereas in an acidic solution (pH4) the DDVP absorption spectrum does not change during many hours, in an alkaline one (pH 9-10), it decreases quickly at $\lambda = 200$ nm concomitantly with the increase of the absorbance at $\lambda = 212$ nm, characteristic to its hydrolysis phosphated products: DMP and DVMP (fig. 1a and b).

We put into evidence the presence of methanol by using a color reaction with chromotropic acid[9] and observed that the higher the pH, the deeper the color ring in solution. This experiment serves as a new argument for a base-catalyzed reaction of DDVP hydrolysis by route II. One can also observe that the absorbance at $\lambda = 212$ nm in alkaline solution (fig 1b) decreases quickly, which attests the instability of these hydrolysis products. For example Scheme (2) explains this behaviour exemplified by DVMP hydrolysis:



Monomethyl phosphoric acid MMP and dichlorvinyl alcohol DCVA are formed in the system. The last one reaches quickly an equilibrium with DCA as follows in (3):



In scheme (1), it first forms DCVA too, but due to the above equilibrium it passes into DCA. We calculated ΔH formation of both equilibrium partners and found[10]: $\Delta H_{\text{DCVA}} = -44.4$ Kcal/mol and $\Delta H_{\text{DCA}} = -51.6$ Kcal/mol which shows the tendency of the equilibrium shifting towards DCA. Our spectrophotometric measurements bring three arguments in favour of scheme I and scheme II in alkaline solutions, namely:

- the appearance of methanol in solution
- the absence of Cl⁻ which demonstrates that DCA as well as DVMP do not liberate this anion.
- MMP is a stable and also toxic hydrolysis product, which explains why we did not find PO_4^{3-} group in the solution.

We were interested in establishing what the bond is which cleaves in DDVP molecule by hydrolysis. In this aim we calculated the bond orders and, as figure 2 shows, we

found that the lowest value (0,61) belongs to phosphate-dichlorvinyl bond, so that it has to cleave first by hydrolysis.

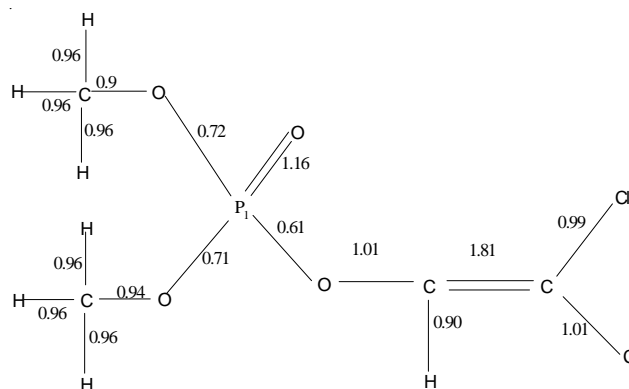


Fig. 2. The bond orders in DDVP molecule

The ion OH⁻ attaches to the phosphorus atom, and the proton to the vinyl fragment, forming DMP and DCA respectively, according to route I as scheme I pointed out. From figure 2 one notices also that the second weak bond in DDVP molecule is between the P atom and the methoxy group (0,71). It cleaves by a similar mechanism when it forms DVMP and methanol, as route II indicates. We calculated also the bond orders in the DVMP molecule (fig. 3), which is in good agreement with scheme II.

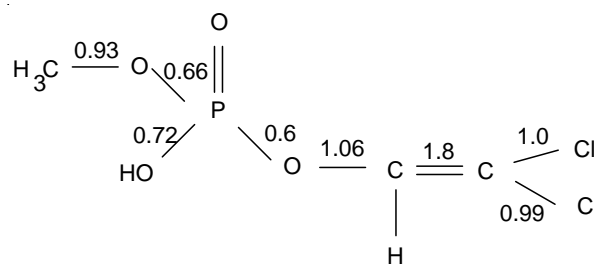


Fig. 3. The bond orders in DVMP molecule, one of the hydrolysis products

Our calculations offer theoretical support for a base-catalyzed reaction of the hydrolysis mechanism.

We carried out our experiments dissolving DDVP in aqueous solutions of different pHs resulting from H₂SO₄ or

NaOH addition. When the initial pH is higher than 4, one observes a decrease of pH during the first 75 s after DDVP addition, so that one measures a ΔpH as figure a indicates.

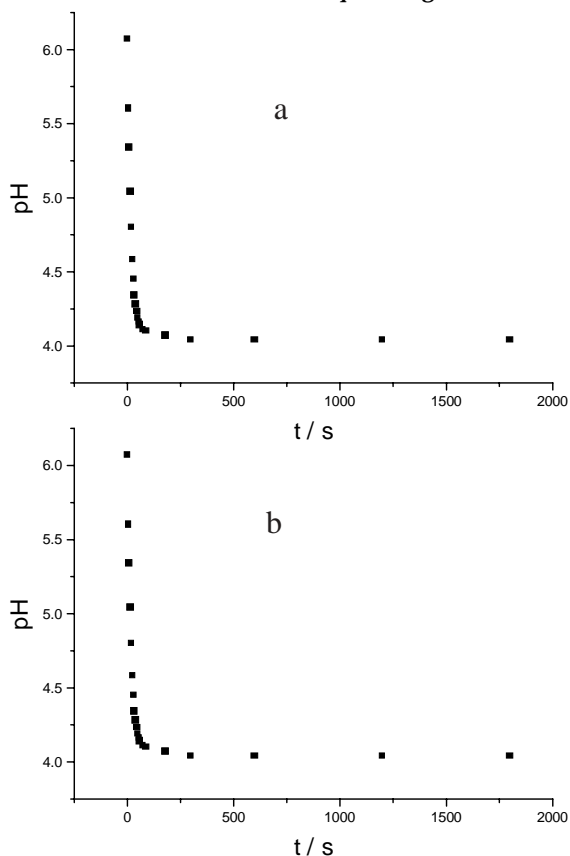


Fig. 4. a) The pH and b) the potential E decrease vs time, after DDVP addition at $pH_0=6$

ΔpH increases with the initial pH of the solution and reaches a maximum value for a $pH_0 = 6$. What is the reason for an increase in H^+ concentration? We explain this behaviour by DCA hydrolysis, an acid-catalyzed reaction with HCl elimination. If this assumption is true, we had to find Cl^- ions in solution. Indeed, using a sensor electrode for Cl^- ions, we found the behaviour described in figure 4b, which attests our above supposition.

When the initial pH of the aqueous solution is higher than 6, ΔpH as well as ΔE decrease as the initial pH_0 increases. In figure 5, a and b, we present the variation of ΔpH and ΔE with the initial pH of the solution:

At the first sight, the behaviour is the same in both cases, namely a curve with a maximum at $pH \sim 6$, due to DCA hydrolysis. However, at a close look, one notices that at high pH_0 (9-10), ΔE is zero because DCA hydrolysis is stopped and there are no Cl^- anions in solution. In exchange ΔpH still has a measurable value at these high pH s. We assigned this behaviour to the presence of other acids that appeared from the hydrolysis mechanism: DMP, DVMP and MMP, the last one being the strongest acid. We have to keep in mind that the presence of these acids as well as the hydrolysis of DCA superposes on DDVP hydrolysis. It is for the first time that such an analysis on DDVP hydrolysis is presented in literature. We calculated in this case a total rate constant from the slope of the linear plot $\log([H^+]_{\infty} - [H^+]_t)$ vs. time, exemplified in figure 6 for $pH_0 = 6$.

It is a pseudo first order rate constant. The plotting of this value vs the initial pH of the solution gives the image of figure 7 with the same shape obtained in figure 4a.

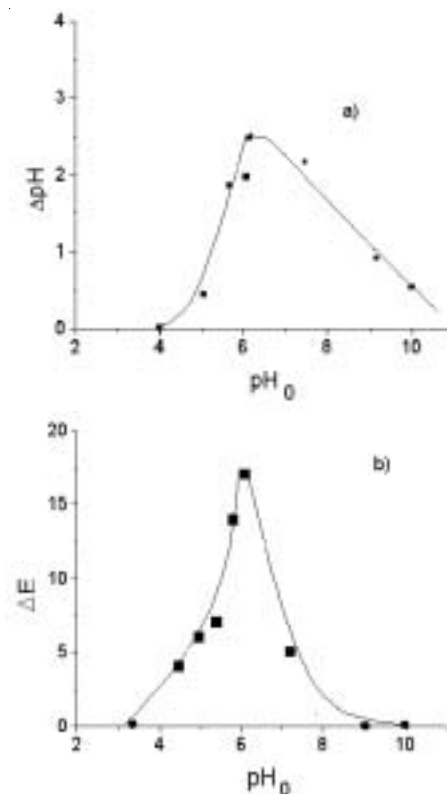


Fig. 5. a) ΔpH vs pH_0 and b) ΔE vs pH_0 ; for $pH_0=6$

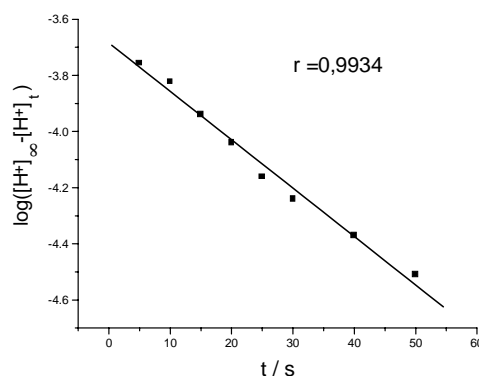


Fig. 6. The first order kinetic of the total hydrolysis.

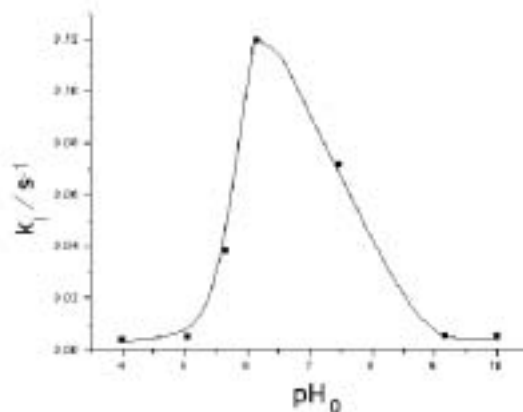


Fig. 7. The variation of the total rate constant k_1 vs pH_0

Conclusion

DDVP hydrolysis in solutions of various initial pH may be described as follows:

- $pH \leq 4$, DDVP hydrolysis does not take place
- pH (4-6), DDVP hydrolysis progresses with increasing pH but accompanied by DCA hydrolysis

-pH (6-10), DCA hydrolysis attenuates until its stopping point, whereas the hydrolysis of DDVP together with DVMP and DMP are favorites, the last hydrolysis product being MMP

-pH ~ 6, is an optimum value of the OH⁻ concentration necessary for the base-catalyzed hydrolysis, as well as of the H⁺ concentration for the acid -catalyzed reaction of DCA.

In conclusion, it is very important to know well the pH value of the contaminated water, because the ratio between DDVP and its hydrolysis products change from one pH to an other, as we demonstrated above. Such information is necessary for the choosing of an adequate pollutant degradation method.

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