

**Research Paper**

## Kinetics and Hydrolysis Mechanism of 2,4-dichlorophenoxyacetic acid

**Jorge Marcelo Romero<sup>1</sup>, Nelly Lidia Jorge<sup>1</sup>, \*Eduardo Alberto Castro<sup>2</sup>**

<sup>1</sup>Área de Química Física Facultad de Ciencias Exactas y Naturales y Agrimensura, UNNE, Avda. Libertad 5460, (3400) Corrientes, ARGENTINA.

<sup>2</sup> INIFTA, Theoretical Chemistry Division, Suc.4, C.C. 16, La Plata 1900, Buenos Aires, ARGENTINA

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**Abstract** - *The hydrolytic transformation kinetics of the 2,4-dichlorophenoxyacetic acid (2,4-D) was investigated as a function of pH. The hydrolysis rate was pH-dependent and the first order. The hydrolysis was much faster in acidic media than under neutral conditions. Two metabolites have been isolated and identified. At all pH values studied, the primary pathway of degradation was the cleavage of the methoxyl oxygen bond.*

**Keywords:** 2,4-dichlorophenoxyacetic acid, UV spectroscopy, herbicide.

### Introduction

Although the benefits generated by the application of agro-chemicals are evident in terms of increased agricultural productivity and improved public health through disease control (e.g. malaria, yellow fever, and dengue), the presence of pesticide residues in the soil, water, and air has created potential risks from both a human and a natural environment perspective.<sup>[1-3]</sup>

The phenoxyacetic acid herbicide 2,4-D is used extensively in agriculture residential settings, and public places to control the growth of broadleaf weeds. A series of epidemiological studies has linked exposure to 2,4-D and other phenoxy acid herbicides in the agricultural setting to risk of Health.<sup>[4-10]</sup> 2,4-D possesses the basic chemical structure of the phenoxy family of herbicides, which include: 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T), 2-Methyl-4-chlorophenoxyacetic acid (MCPA), 2-(2-Methyl-4-chlorophenoxy) propionic acids (mecoprop, MCPP), 2-(2,4-Dichlorophenoxy)propionic acid (dichloroprop, 2,4-DP), (2,4-Dichlorophenoxy)butyric acid (2,4-DB).

Different organizations have taken different stances on 2,4-D's cancer risk. On August 8, 2007, the United States Environmental Protection Agency issued a ruling that stated that existing data does not support a conclusion that links human cancer to 2,4-D exposure.<sup>[11]</sup> However, the International Agency for Research on Cancer (IARC) has classified 2,4-D among the phenoxy acid herbicides MCPA and 2,4,5-T as a class 2B carcinogen - possibly carcinogenic to humans.<sup>[12]</sup>

A 1995 panel of 13 scientists reviewing studies on the carcinogenicity of 2,4-D had divided opinions, but the predominant opinion was that it is possible that 2,4-D causes cancer in humans<sup>[13]</sup>. A 1990 study of farmers, even when adjusting for exposure to other chemicals, found that 2,4-D

exposure substantially increased the risk of Non-Hodgkin's lymphoma (NHL).<sup>[14]</sup> A 2000 study of 1517 former employees who had been exposed to the chemical in manufacturing or formulating 2,4-D found no significant increase in risk of mortality due to NHL following 2,4-D exposure, but did find an increase in risk of mortality due to amyotrophic lateral sclerosis.<sup>[15]</sup>

An increased understanding of the environmental fate and behavior of 2,4-D is imperative to reduce their potential negative effects on the agronomic systems. A probable mechanism of hydrolysis of 2,4-D without the complete mineralization is shown in Figure 1, where the products of hydrolysis are 2,4-dichlorophenol and glycolic acid. The main purpose of this study was therefore to explore the mechanism, kinetic reaction of 2,4-D and the nature of degradation products in water operated under sterilized conditions, the effect of increasing of pH was investigated in detail. Figure 1.

### Material and Methods

**Chemicals:** Standard of 2, 4-D was purchased from Sigma-Aldrich. Stock solution of this herbicide was prepared in water. All chemicals were used as received.

**Experimental Systems:** All aqueous solutions were prepared using high purity deionized water. To avoid microbial degradation, all glassware and solutions were autoclaved prior to use. The effect of pH on the kinetics of the 2,4-D hydrolysis was determined in aqueous buffer solutions (pH 4-7) were prepared using citrate buffers for pH 4, acetate buffer for pH 5, phosphate buffer for pH 7.

**Hydrolysis Rate Determination:** The hydrolysis rate was determined by monitoring the disappearance of the 2,4-D in 195.6 ppm aqueous buffer solutions.

A stock solutions containing 1.6 mM were spiked to buffer solutions in serum bottles, yielding initial herbicide concentrations of 195.6 ppm. Bottles were capped with teflon faced butyl rubber septa and incubated at  $25 \pm 0.2$  °C in the dark. At regular time intervals, depending on the hydrolysis rate, aliquots were removed from each bottle and were analyzed directly via UV spectroscopy. All the experiments were run in triplicate.

## Results and Discussion

The time courses for hydrolysis of this herbicides at pH 4, 5, 6 and 7 are depicted in Figure 2, which represent their hydrolytic transformations in acidic, and neutral media. As shown in Figure 2, the dissipation of 2,4-D was slower at neutral pH than at acidic pH. This result suggests that this compound is more susceptible to chemical hydrolysis in acidic solutions than in neutral media.

The hydrolysis of 2,4-D in the pH range 4-7 followed simple first-order kinetics (Table 1 and Figure 2). The reaction was quite fast at acid pH and much slower at neutral pH. Noticeably, a drastic decrease of the rate constant was observed from pH 6 to pH 7, most likely due to a mechanism change. In fact, they indicated that the disappearance of 2,4-D at 25 °C from pH 4 to pH 7 was of first-order and that 2,4-D was more persistent at neutral than at acidic pH. (Figure 2)

**Table 1: Kinetics data of hydrolysis of 2,4-D at different pH values**

pH	$k \times 10^3 (d^{-1})$	$t_{1/2} (d)$	Correl coeff
4	7.5	92	0.988
5	10.5	66	0.996
6	5.6	124	0.987
7	2.8	247	0.979

Therefore, small changes in pH would affect the neutral/anionic form ratio for the herbicide, particularly near its pKa.

For 2,4-D, two primary products were detected and identified in acidic and neutral solutions: Glycolic acid **2** and 2,4-dichlorophenol **3** arise from the hydrolytic cleavage of the methoxyl oxygen bond.

The product distribution in 2,4-D hydrolysis at different pH values is reported in Figure 3. In the pH 4 the products **2** was the minor metabolites with major amounts of **3**. At pH 5 both products are obtained in the same concentration. In pH 7 the products **2** was the minor metabolites with major amounts of **3**.

At pH 6, 2,4-D is totally in anionic form, less suited to the nucleophilic attack by water; therefore, the hydrolysis rate decreases. Metabolites **2-3** are formed, but the absence of an effective acid catalysis does not permit further degradation of products **2** and **3**. (Figure 3)

The concentrations of these two products increased gradually with the dissipation of the corresponding parent compound. Like all phenoxy acids, the cleavage of the methoxyl oxygen bond was a predominant hydrolysis

pathway for 2,4-D, especially in acidic water and soils.

In this case, the hydrolysis process occurs through an electrophilic and nucleophilic attack of H<sub>2</sub>O to the methoxyl oxygen y and metilen group, respectively, producing **2** and **3**. (Figure 1)

## Conclusion

The results indicate that the rate of hydrolysis of 2,4-D is pH-dependent. At all values of pH studied, the primary pathway of degradation is the cleavage of methoxyl oxygen bond.

The herbicidal activity and potential environmental effects of these daughter products should be considered to provide a better understanding of the environmental effects of these family herbicides.

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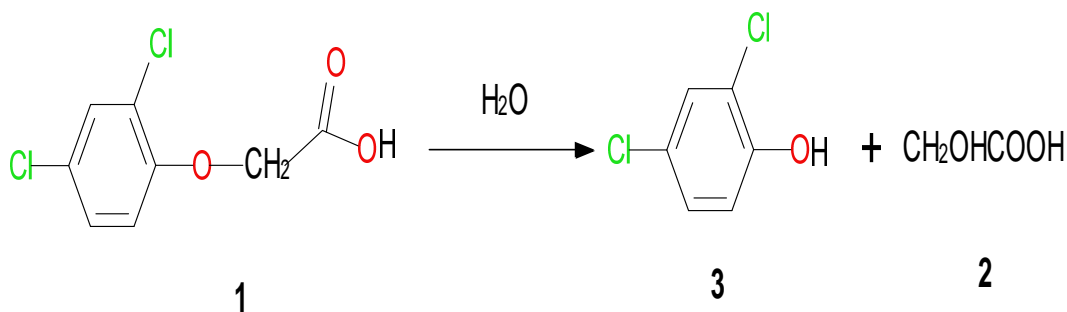


Figure 1: Molecular structures of 2,4-D and hydrolysis pathway.

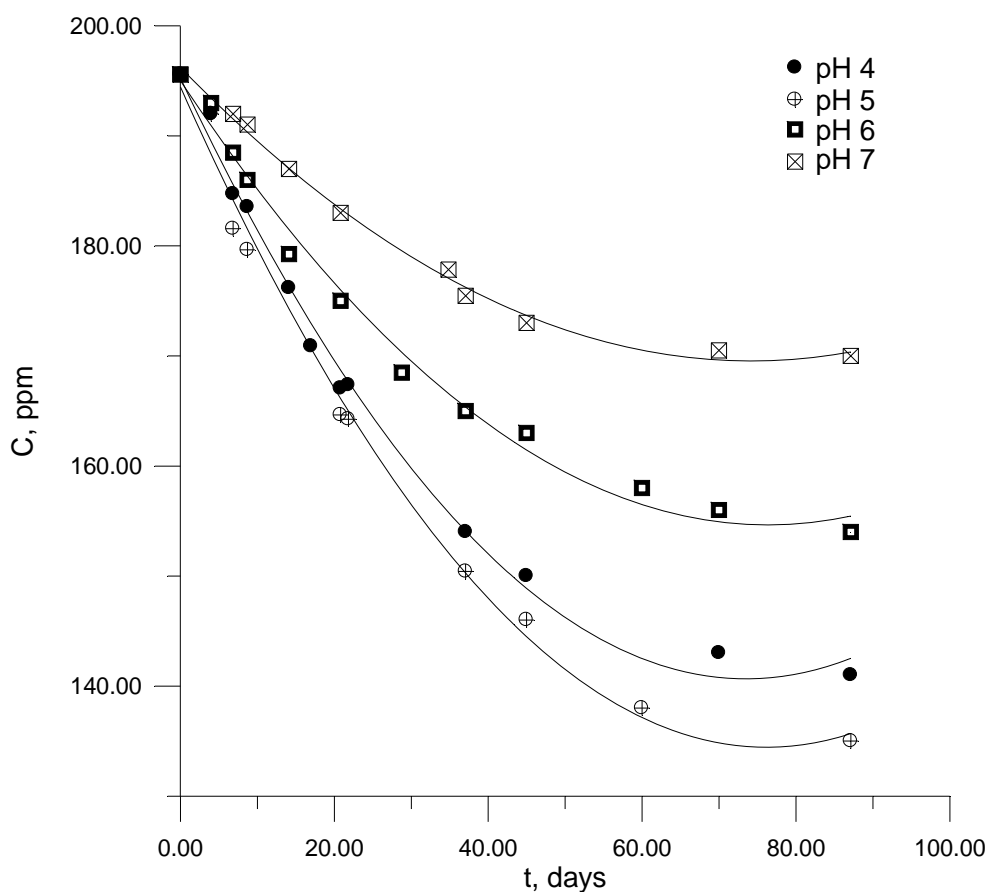


Figure 2: Disappearance of 2,4-D at different pH values.

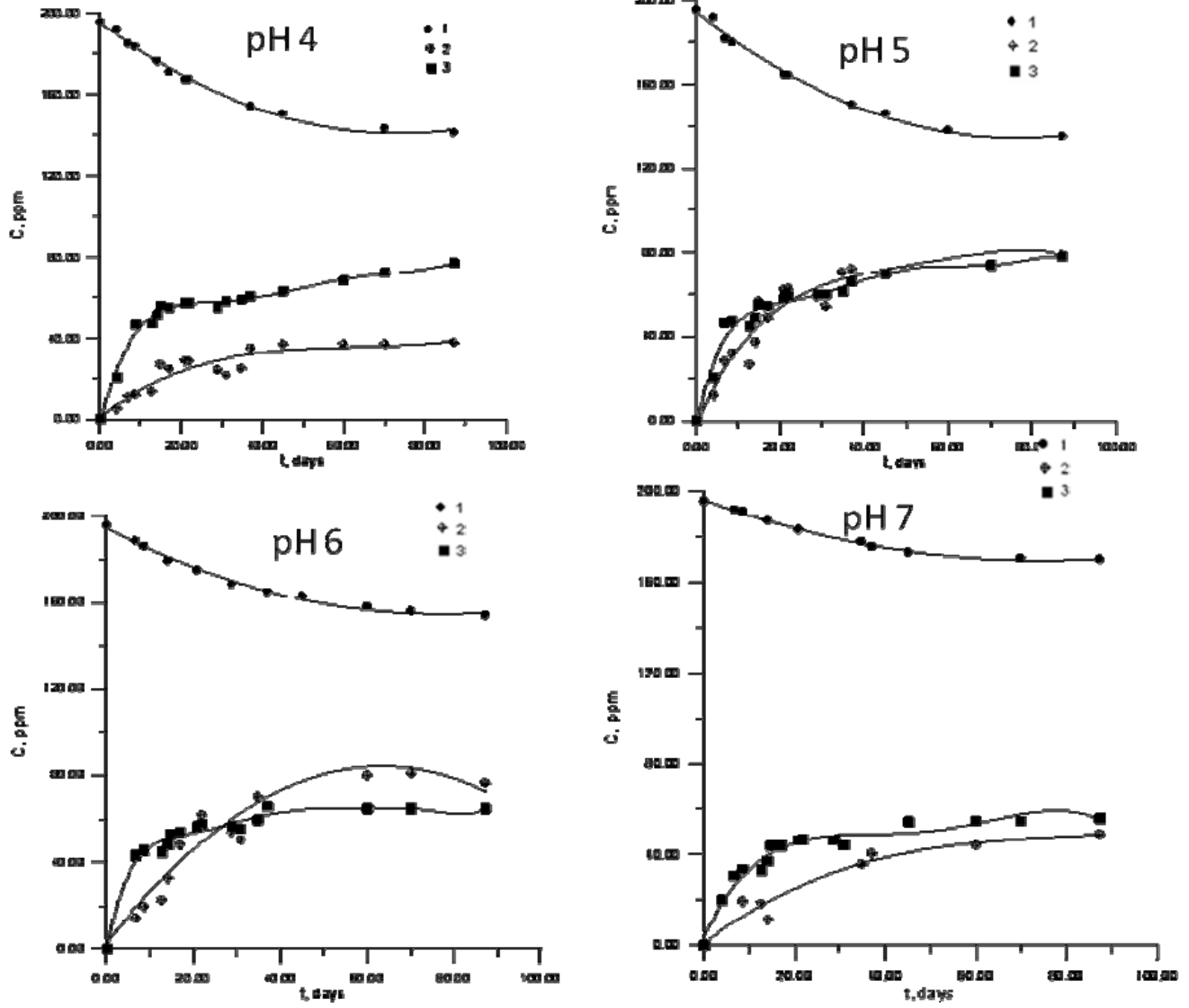


Figure 3: Product distribution at different pH values