

Stability and Decomposition Study of Ethoprophos in Emulsifiable Concentrates during Storage.

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■ ABSTRACT

The present study evaluated the chemical stability of ethoprophos, formulated as a 72% w/v emulsifiable concentrate, under different preparation and storage conditions, with the aim of determining the conditions most favorable for maintaining the concentration of the active ingredient. Four experimental solutions with different compositions and pH values were prepared, incorporating an organosilicone adjuvant, citric acid, or a KOH solution, in addition to an additive-free control, and were stored under ambient and accelerated conditions of 40 °C and 75% relative humidity, following the CIPAC MT 46.4 procedure. Ethoprophos concentration was determined by gas chromatography with a flame ionization detector (FID) on days 0, 1, 4, 8, and 15. The results showed a progressive decrease in the active ingredient in all solutions, although at different rates depending on the pH and composition of the mixture. The highest relative stability was observed under conditions close to neutral pH, whereas alkaline media exhibited more rapid degradation, mainly due to base-catalyzed hydrolysis; likewise, acidic conditions favored acid-catalyzed hydrolysis. Consequently, maintaining ethoprophos under conditions close to pH 6–7 and avoiding additives or extreme chemical conditions was found to favor its stability and reduce active ingredient degradation during emulsion preparation and storage.

■ INTRODUCTION

Ethoprophos (CAS: 13194-48-4) is an organodithiophosphorus insecticide belonging to the organophosphate group and is commonly formulated as an emulsifiable concentrate (EC). It is used primarily for the control of soil insects, including symphylans. The chemical stability of this type of molecule is highly dependent on the pH of the medium and the presence of adjuvants, fertilizers, and other components that may modify the chemical environment of the emulsion during preparation and the period prior to application.

Organophosphates are known to be susceptible to acid- and base-catalyzed hydrolysis processes, arising from the electrophilic nature of the phosphorus atom and the oxygen atoms of the phosphate group. Therefore, variations in pH, as well as the presence of complexing

agents, organic salts, or strong bases, can accelerate the degradation of the active ingredient and affect its agronomic efficacy.

The aqueous degradation of ethoprophos is determined by the pH of the medium and temperature, showing high stability under acidic and neutral conditions compared with accelerated decomposition under alkaline conditions. At moderate temperatures (20–25 °C), the compound is highly resistant to hydrolysis over the pH range of 3 to 7, with half-lives ranging from 28 to 39 weeks (pH 3–6) and prolonged stability at pH 5 and 7. However, as the pH increases to 9, the hydrolysis rate increases drastically, reducing the half-life to a range of 39 to 83 days at 20–25 °C, and decreasing to only 10–14 days when the temperature increases to 35 °C. This kinetic behavior confirms that the main degradation pathway in aqueous solution is the nucleophilic attack of the hydroxide ion

(OH⁻) on the central phosphorus atom, a thermally favored process that accelerates the decomposition of the molecule into by-products referred to as secondary metabolites.

Analysis of the by-products generated in the experiments demonstrates that hydrolysis occurs through the selective cleavage of the ester and thioester bonds of the organophosphorus group. Cleavage of the phosphate bond generates experimentally identified compounds, such as *O*-ethyl *S*-propyl phosphorothioic acid through the loss of a propylthio chain, or alternatively, the formation of ethanol and *S,S*-dipropyl phosphorodithioic acid. Likewise, under severe alkaline conditions (pH 9) and at higher temperature (35 °C), volatilization of up to 40% of the initial radioactivity has been reported in the form of low-molecular-weight volatile derivatives. Overall, these findings demonstrate that water acts not only as a solvent but also as an active nucleophilic reagent that progressively decomposes ethoprophos.

The present study aimed to evaluate the stability of ethoprophos formulated as an emulsifiable concentrate under different emulsion preparation conditions, considering the effects of pH, the use of an organosilicone adjuvant, the addition of a potassium hydroxide-based fertilizer, and storage conditions, in order to identify the range providing the highest chemical stability of the active ingredient.

■ EXPERIMENTAL

Equipment and reagent:

In all tests, an emulsion simulating actual agricultural application conditions was prepared using:

- 5 L of water.
- 10.5 mL of 72% w/v ethoprophos-based emulsifiable concentrate.

- Binder Stability Chamber, Serial No. 13-05885, Model KBF240-ULE5.

Based on this formulation, four experimental solutions were prepared:

Solution 1:

- Organosilicone adjuvant (1.25 mL).
- Citric acid (3.5 g).
- pH adjusted to between 5.0 and 5.5.

Solution 2:

- Organosilicone adjuvant.
- pH adjusted to 7.0.

Solution 3:

- Organosilicone adjuvant.
- KOH reactive solution.
- pH adjusted to 8.0 using a strong base.

Solution 4 (relative control):

- No organosilicone adjuvant.
- No KOH.
- No citric acid.
- Initial pH of 5.0.

Each solution was prepared in five independent replicates.

Storage conditions

The solutions were evaluated under two conditions:

- Stability chamber (40°C/75% relative humidity).
- Retain warehouse (normal storage conditions).

Análisis instrumental de etoprofós.

Instrumental analysis of ethoprophos

Analytical determinations of the active ingredient content were performed on days 0, 1, 4, 8, and 15 after emulsion preparation. Analysis was performed by gas chromatography (GC) with a flame ionization detector (FID), using an HP-1, HP-5, or equivalent capillary column. A 1 µL aliquot of the sample, previously diluted in HPLC-grade methanol, was

injected. The oven, injector, and detector temperatures were set at 220 °C, 260 °C, and 280 °C, respectively. Hydrogen, air, and nitrogen were used as carrier and detector gases at flow rates of 60, 50, and 50 mL/min, respectively, with an analysis time of 3 min per injection.

The stability study was conducted under accelerated conditions following the **CIPAC MT 46.4: Accelerated Storage Procedure** over a period of 15 days to evaluate the behavior of the active ingredient under the different experimental conditions.

■ RESULTS & DISCUSSION

The results obtained were tabulated and presented graphically to assess the degradation of ethoprophos under different acidity conditions. The results are presented below:



Figure 1. Ethoprophos concentration in Solution 1 throughout the study.

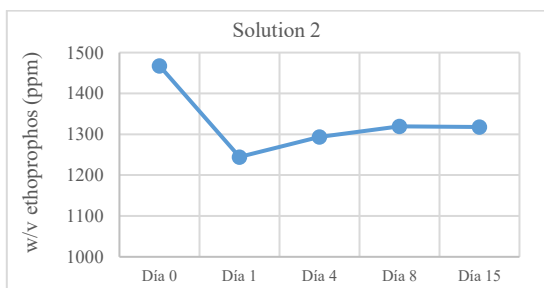


Figure 2. Ethoprophos concentration in Solution 2 throughout the study.

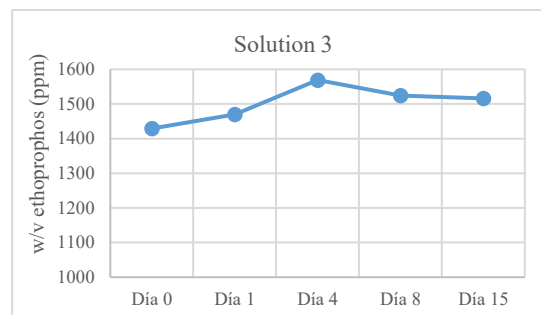


Figure 3. Ethoprophos concentration in Solution 3 throughout the study.

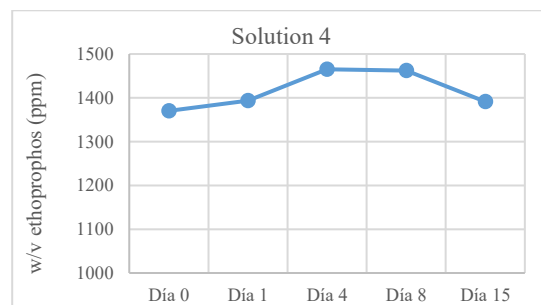
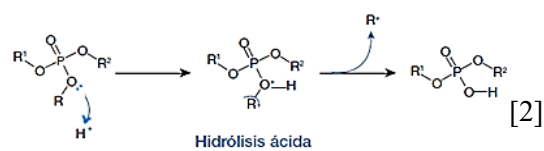
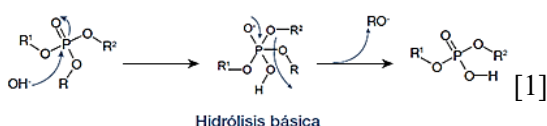


Figure 4. Ethoprophos concentration in Solution 4 throughout the study.

General degradation trend

A progressive decrease in ethoprophos concentration over time was observed in all solutions, which is consistent with chemical degradation processes occurring in aqueous media. However, the extent and rate of degradation varied significantly depending on the composition of the mixture and the initial pH. A relevant finding was that, regardless of the initial pH, all solutions converged toward a pH close to 6 after 15 days, suggesting the establishment of a chemical equilibrium between ethoprophos, its degradation products, and the aqueous medium. From an agricultural chemistry perspective, organophosphorus pesticides classified as esters or amides of phosphoric, thio-phosphoric, di-thiophosphoric, phosphonic, or phosphinic acids generally exhibit lower

environmental persistence due to their susceptibility to chemical and hydrolytic degradation processes. This same susceptibility contributes to establishing pre-harvest intervals, application rates, and sequential application schedules in crops. The stability and degradation dynamics of these compounds in aqueous solution are strongly influenced by the pH of the medium. Under alkaline conditions ($\text{pH} > 7.0$), the primary degradation pathway is base-catalyzed hydrolysis, which occurs through nucleophilic attack by the hydroxide ion (OH^-) on the central phosphorus atom. In acidic media ($\text{pH} < 7.0$), degradation proceeds through acid-catalyzed hydrolysis, in which hydronium ions (H_3O^+) interact with the lone electron pairs of oxygen, promoting cleavage of the O–R ester bonds in the organophosphorus compound (see Equations 1 and 2).



Effect of pH and Composition

Solution 1: This solution showed moderate degradation of the active ingredient, with a noticeable decrease after day 4 and a more pronounced reduction by day 8. The slightly acidic medium, enhanced by the addition of citric acid, favors acid-catalyzed hydrolysis of ethoprophos. In this mechanism, hydronium ions act as electrophiles toward the oxygen atoms of the phosphate group, weakening the P–O bonds and facilitating molecular cleavage.

The presence of the adjuvant did not appear to provide additional stability. Moreover, because it is a product designed to enhance foliar adhesion, its inclusion in a soil-applied insecticide is not necessarily justified and could potentially affect the stability of the emulsion.

Solution 2: This solution exhibited better relative stability compared with the acidic and alkaline conditions. A neutral pH reduces both acid- and base-catalyzed hydrolysis, allowing the active ingredient concentration to be maintained for a longer period. The mean and median values indicate a more gradual and less abrupt degradation than that observed in solutions under more extreme pH conditions. This behavior supports the hypothesis that near-neutral pH conditions are more favorable for ethoprophos stability.

Solution 3: This solution exhibited an unfavorable stability profile, with significant active ingredient losses occurring at early stages of the study. The alkaline pH favors base-catalyzed hydrolysis, in which hydroxide ions, acting as strong nucleophiles, attack the electrophilic phosphorus atom and accelerate cleavage of the phosphorus-containing bonds. Additionally, the presence of potassium hydroxide further increases the concentration of hydroxide ions, thereby promoting degradation processes.

Solution 4 (pH 5 without additives): Despite its acidic conditions, this solution exhibited greater stability than Solution 1, suggesting that the absence of adjuvants and other formulation components reduces potential degradation pathways. Nevertheless, a progressive loss of active ingredient was observed, consistent with acid-catalyzed hydrolysis, although at a lower extent than

in the more complex formulation. Increases in concentration following an initial decrease, such as that observed after the first day in Solution 1, should be interpreted as analytical variability rather than as actual regeneration of ethoprophos. Minor variations in the measured concentration may result from sample preparation, instrumental variability, or other analytical factors. Since hydrolysis is an irreversible degradation pathway under the experimental conditions, an actual increase in the amount of ethoprophos would not be chemically expected.

Overall, the study demonstrates that alkaline hydrolysis of organophosphorus pesticides predominantly proceeds through nucleophilic substitution at the phosphorus atom. The reaction rate is influenced by the accessibility of the phosphorus center and the characteristics of the leaving group, which affect the transition state and facilitate bond cleavage. The kinetic and energetic considerations reported in the consulted literature indicate that the process is favored under alkaline conditions due to the high concentration of OH^- , which promotes nucleophilic attack and accelerates cleavage of P–O or P–S bonds.

This behavior explains the marked instability of organophosphorus compounds at elevated pH and supports alkaline hydrolysis as one of the principal chemical degradation pathways for this type of insecticide. At pH values below approximately 6.0, the predominant pathway shifts toward acid-catalyzed hydrolysis, which generally proceeds through protonation of susceptible functional groups followed by bond cleavage; although the reaction may be slower under some conditions, its effect on the active ingredient concentration remains significant.

Influence of Storage Conditions

The differences between the stability chamber and the retain warehouse did not alter the overall degradation trend but did influence data variability. This indicates that, although environmental conditions may accelerate or retard degradation, the predominant factors controlling ethoprophos stability under the conditions evaluated are the chemical composition of the mixture and its pH.

Other Degradation Pathways

Studies conducted in soil have shown that ethoprophos may undergo several dissipation processes, including anaerobic degradation, adsorption–desorption, leaching, photolysis, and, predominantly, aerobic degradation. In surface aquatic environments or at soil interfaces exposed to solar radiation, ultraviolet radiation can promote photodegradation processes through the generation of reactive oxygen species and other radical species. These reactions can modify the structure of the compound, including oxidation of sulfur and cleavage of ester and thioester bonds, resulting in more polar derivatives with greater water solubility and lower environmental persistence. From a biological perspective, microbial biodegradation and enzymatic transformation represent additional dissipation pathways mediated by soil bacteria and fungi. Specialized enzymes, including bacterial phosphotriesterases (PTEs) and cytochrome P450 monooxygenases, can catalyze transformations involving the phosphorus–sulfur (P–S) and phosphorus–oxygen (P–O) bonds characteristic of organophosphorothioate compounds. Microbial metabolism can transform ethoprophos into intermediate metabolites, including *O*-ethyl *S*-propyl

phosphorothioic acid and *S,S*-dipropyl phosphorodithioic acid, facilitating their subsequent transformation and, under suitable conditions, further degradation toward inorganic products.

■ CONCLUSIONS

Ethoprophos in emulsifiable concentrate formulations exhibits maximum stability within a pH range close to 6–7, toward which the solutions tend to shift over time.

Both acidic and alkaline conditions accelerate degradation of the active ingredient through acid- and base-catalyzed hydrolysis, respectively. The organophosphorus nature of ethoprophos explains this behavior, given that:

- The phosphorus atom acts as an electrophilic center toward nucleophiles such as OH^- .
- The oxygen atoms of the phosphate group are susceptible to interaction with hydronium ions (H_3O^+).

The incorporation of organosilicone adjuvants and alkaline solutions does not improve stability and, in some cases, may negatively affect it, particularly when combined with extreme pH conditions. From a technical and good-practice perspective, pH should be controlled within the optimal range during emulsion preparation. When combining ethoprophos with other agrochemicals, fertilizers, or adjuvants, preparation of a small-scale compatibility test is recommended before preparing the full spray mixture. Combination with highly oxidizing agents or strongly acidic substances is not recommended.

As an environmental consequence of its chemical properties, the reported high rate of aerobic mineralization indicates that ethoprophos may exhibit relatively low persistence in well-aerated soils, a characteristic generally associated with many organophosphorus pesticides compared with more persistent organochlorine compounds.

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