



Photolysis under sunlight irradiation and buffer solution acid of herbicide safener Mefenpyr-diethyl: an analytical and GC/MS investigation

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Abstract

Photolysis of the herbicide safener Mefenpyr-diethyl by sunlight irradiation in aqueous buffer solution (pH 4.4) was investigated by Gas Chromatography /Mass Spectra (GC/MS). Photodegradation of mefenpyr-diethyl was observed at investigated pH. Photodegradation rate followed first-order kinetics with significant correlation coefficient. The t_{1/2} value was 2.69 h. Four metabolites were detected and identified according to GC-MS spectral data. Photoproducts PP1 and PP2 show their maximum intensities after 3 h of irradiation after which they also began to degrade into metabolites PP3 and PP4. To our knowledge, the photoproducts PP2 and PP4 were detected previously in mefenpyr-diethyl hydrolysis and photolysis process.

1. Introduction

Mefenpyr-diethyl, also known as “antidote”, is usually used as an herbicide safener in combination with other herbicides over cereal grain crops to improve herbicide selectivity between crops and weed species [1-3]. Pesticides in contaminated natural water can undergo transformation by different degradation processes such as microbial, and photochemical processes [4-6] the formed metabolites were sometimes more toxic than the parent compound [7]. Photochemical transformation is one of the main abiotic degradation pathways occurring in natural waters and one of the factors controlling the fate of pesticides in the environment [6-9]. Phototransformation of pesticides proceeds with different pathways through direct and indirect photolysis. Direct photolysis can occur if the concerned pesticide absorbs UV-Visible light, while indirect photolysis of the pesticide compound can be induced by chemical components in the aquatic environment such as dissolved organic matter, nitrate, hydrogen peroxide and iron species [10-12]. The time and type of degradation of pesticides (direct and indirect) are two important factors that govern the efficiency and safety of these xenobiotics [13]. In literature, one study concerning the photodegradation of this herbicide under natural sunlight irradiation and buffer solution pH 6.9 was reported [15]. This paper presents the rate of photolysis and nature of photoproducts of mefenpyr-diethyl formed in aqueous buffer solution acid (pH 4.4) under natural sunlight conditions.

2. Material and Methods

2.1 Chemicals

Mefenpyr-diethyl (Figure 1) was supplied by Sigma–Aldrich (Germany) as analytical standards with purity >97%. Stock solution of mefenpyr-diethyl dissolved in methanol was established at a concentration of 100 mg/L. Solvents were high-performance liquid chromatography (HPLC) grade (methanol, dichloromethane). Anhydrous sodium sulfate was analysis grade. Phosphate buffers (KH₂PO₄ and K₂HPO₄) were also purchased from Aldrich. Milli-Q quality water (Millipore, Bedford, MA) was used to prepare the buffer solution. All stock solutions were stored in a refrigerator at 4°C. The physicochemical properties of Mefenpyr-diethyl are cited in table 1.

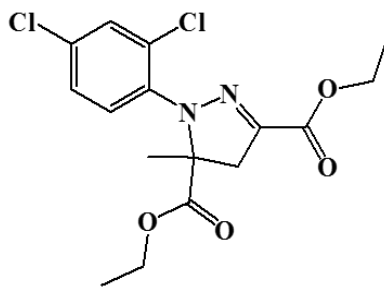


Figure 1: Chemical structure of MFD (Mefenpyr-diethyl)

Table 1: Some important physicochemical properties of Mefenpyr-diethyl

IUPAC: diethyl (RS)-1-(2,4-dichlorophenyl)-5-methyl-2-pyrazoline-3,5-dicarboxylate	
Molecular Weight	373.23(g/mole)
Molecular formula	C ₁₆ H ₁₈ Cl ₂ N ₂ O ₄
purity	99.2%
Solubility in water (pH= 6,1; 25°C)	20mg/L
Solubility in dichloromethane	500 g/L
Solubility in methanol	400 g/L
UV/visible (nm)	Primary Amax = <200 Secondary Amax = 305

2.2 Photolysis experiment

Mefenpyr-diethyl photolysis experiment under sunlight was conducted in open air on June 16, 2014 in ENS institute, Rabat, Morocco (latitude 34.1 °N) from the time period between 9.00 a.m. and 6.00 p.m, at temperature 32°C. The kinetic experiment was performed by following the disappearance of mefenpyr-diethyl as well as the formation of its degradation products using GC-MS. The buffer solution at pH 4.4 was prepared by dissolving KH₂PO₄ and K₂HPO₄ in Milli-Q quality water. Mefenpyr-diethyl (stock solution) was added into buffer solution to achieve an initial concentration at 2 mg/L. The aqueous buffer solutions (100 mL) were transferred into six 10 mL glass tubes. All six tubes were immediately sealed and then placed under the irradiation of sunlight in open air. Irradiation times were 0.17, 1, 3, 6 and 9h. 2 mL aqueous buffer solution sample were removed at intervals and extracted with dichloromethane for three times (3×5 mL). The combined extracts were dehydrated on anhydrous sodium sulfate Na₂SO₄ and then evaporated to dryness and dissolved in 100 µl of methanol for GC/MS analysis. The experiment was performed in duplicate.

2.3 GC/MS analysis

The GC/MS analysis was carried out on Perkin Elmer Clarus Autosystem Gas Chromatograph/Turbomass Mass Spectrometer instrument operating in electron impact (EI) ionization mode at 70 eV, with MS transfer line temperature: 280 °C, ion source temperature: 230 °C, quadrupole temperature: 150 °C. In the full-scan mode, the scanned mass range was 50–400 amu with a scan rate of 1.56 scans /s. Solvent delay was set to 5 min. An HP-5MS column (Hewlett Packard, Palo Alto, CA, USA) (30 m×0.25 mm×0.25 µm) was used. The flow rate of the carrier gas (He) was 1 mL/min. The temperature program was 100 (1 min isotherm) to 260°C, ramped at 15 °C/min and hold at the final temperature for 3 min. Injector temperature was 210 °C. The mode of inlet was split 1/20 and the injected volume was 1 µL. The total time of analysis was 14.65 min. The identification of the different photolysis products were confirmed by comparing the measured mass spectral data with those obtained from the library Nist, as well as literature data [2,3,14,15].

3. Results and discussion

3.1 Identification the metabolites of mefenpyr-diethyl

In the present study a GC-MS procedure was applied to identify the four photolysis products of irradiated herbicide mefenpyr-diethyl in buffer solutions at pH 4.4. Five compounds showed the characteristic mass spectral fragmentation of the pesticide mefenpyr-diethyl and their metabolites (Figure 2). The parent compound mefenpyr-diethyl appeared at retention time 13.28 min and four photoproduct PP1 (13.95 min), PP2 (12.95 min), PP3 (12.60 min), and PP4 (13.60min) identified according their fragmentation pattern reported in the literature

[15] as indicated in Table 2. The (Figure 3) showed the chemical structures of the four photoproducts of mefenpyr-diethyl.

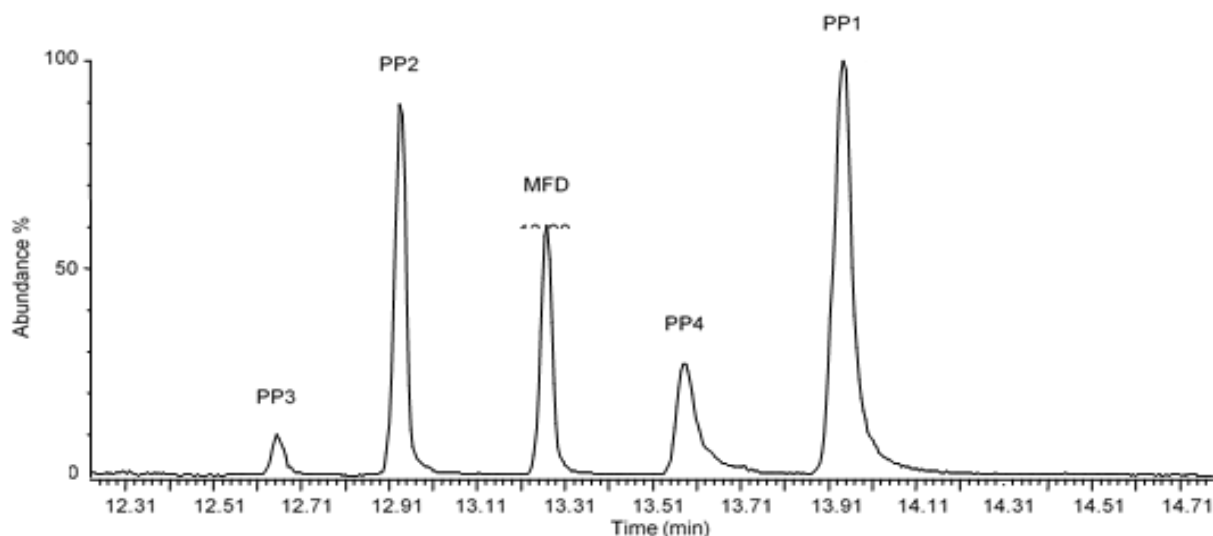


Figure 2: Analytical chromatogram of mefenpyr-diethyl and these photoproducts

Table 2: GC-MS analysis of metabolites of MFD in aqueous buffer solution pH 4.4 under sunlight (Base peaks are printed in bold). RT: Retention time; PP= photoproduct

Compound	RT [min]	[M] ⁺ /base peak (m/z)	Characteristic ions
Mefenpyr-diethyl (MFD)	13.28	372/ 253	327, 301, 299, 257, 255, 253, 229, 227, 188, 186, 165, 145, 124, 75.
PP₁ O ₅ -ethyl O ₃ -methyl 1-(2,4 dichlorophenyl) 5-methyl-4H-pyrazole-3,5-dicarboxylate	13.95	358/ 253	327, 289, 287, 285, 257, 255, 253, 241, 186, 165, 145, 124, 109, 75.
PP₂ O ₃ -ethyl O ₅ -methyl 1-(2,4-dichlorophenyl)-5-methyl-4H-pyrazole-3,5-dicarboxylate	12.95	344/ 253	327, 274, 272, 270, 257, 255, 253, 227, 188, 186, 145, 124, 109, 57.
PP₃ 2-(2,4-dichlorophenyl)-5-methoxycarbonyl-3-methyl-4H-pyrazole-3-carboxylic acid	12.60	330/ 253	313, 296, 274, 272, 270, 257, 255, 253, 227, 188, 186, 145, 124, 57.
PP₄ 1-(2,4-dichlorophenyl)-5-methoxycarbonyl-5-methyl-4H-pyrazole-3-carboxylic acid	13.60	316/ 253	313, 287, 285, 281, 262, 255, 253, 227, 188, 186, 145, 124, 109, 57.

3.2 Kinetic photolysis of mefenpyr-diethyl

Mefenpyr-diethyl has strong absorbance at 200–400 nm (Figure 4), making it susceptible to sunlight irradiation [2,3].

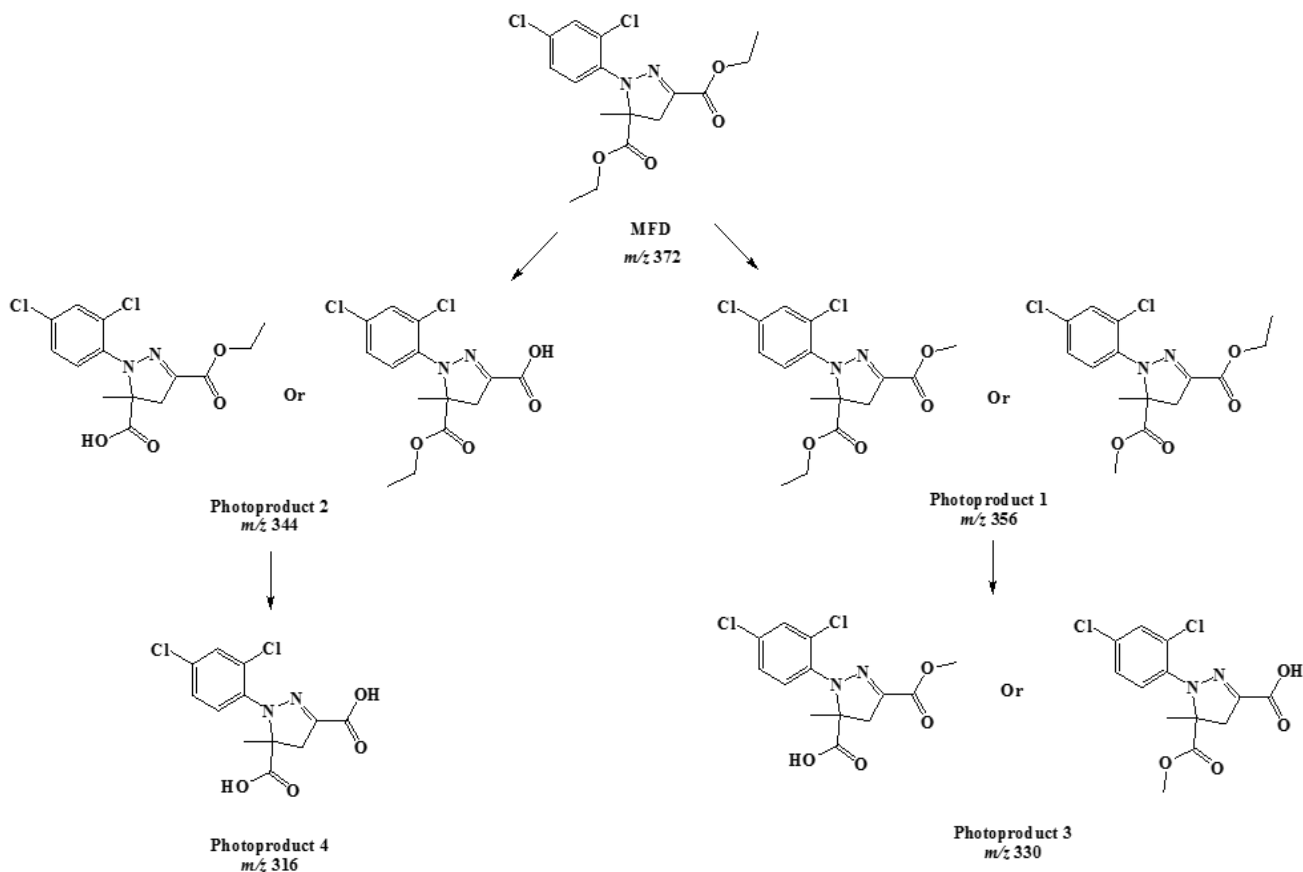


Figure 3: The possible photolysis pathway of mefenpyr-diethyl in aqueous buffer solution (pH 4.4) under sunlight

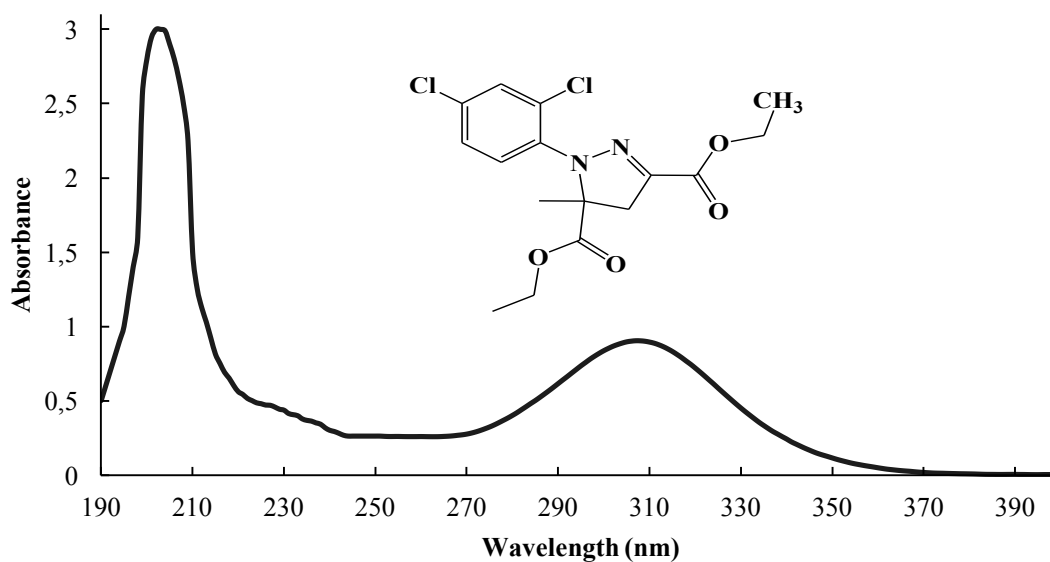


Figure 4: Absorption spectrum of the mefenpyr-diethyl.

The photolysis experiment of mefenpyr-diethyl was carried out in aqueous buffer solution at pH 4.4 since the hydrolysis of mefenpyr-diethyl take place at $pH \geq 7$ [3]. Notable photolysis of mefenpyr-diethyl was observed under sunlight irradiation at investigated pH. The degradation of mefenpyr-diethyl was 6.80, 31.3 and 52.83 % of herbicide disappeared after 0.17, 1 and 3h, respectively. A linear correlation between $\ln C_t$ and t was obtained with a regression coefficient R^2 greater than 0.99 (Figure 5), demonstrating that the first-order kinetics was followed. The half-life value was calculated from the regression equation. The rate constants (k), half-life ($t_{1/2}$) values and R^2 of mefenpyr-diethyl in buffer solution are given in (Table 3).

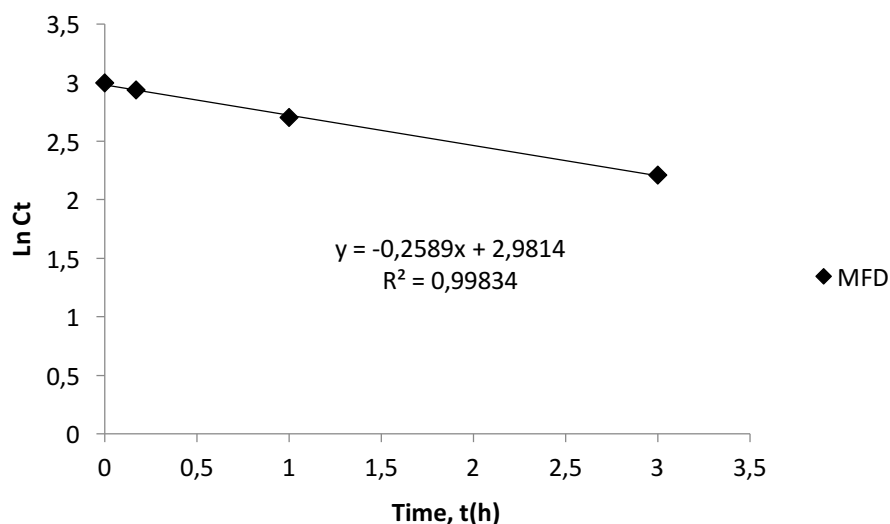


Figure 5: First order rate of mefenpyr-diethyl photolysis at pH 4.4. Points are the means of experiment data. Line is linear regression result.

Table 3: Rate constant, half-life and R^2 values for mefenpyr-diethyl in buffer solution pH 4.4

Buffer solution	pH	Rate constant, $k (h^{-1})$	Half-life, $t_{1/2} (h)$	Regression coefficient, R^2
Under sunlight	4.4	0.258	2.69	0.998

The comparison of the values of the rate constant and the half time with the results found for a pH 6.9 [15], shows that the rate constant increases with increasing pH and half time decreases with increasing pH. The photolysis of mefenpyr-diethyl is notable in neutral medium.

The photodegradation of mefenpyr-diethyl in buffer solution pH 4.4 is presented in (Figure 6) with the evolution of four different photoproducts. We estimated the change in the amount by analysis of the area of every product.

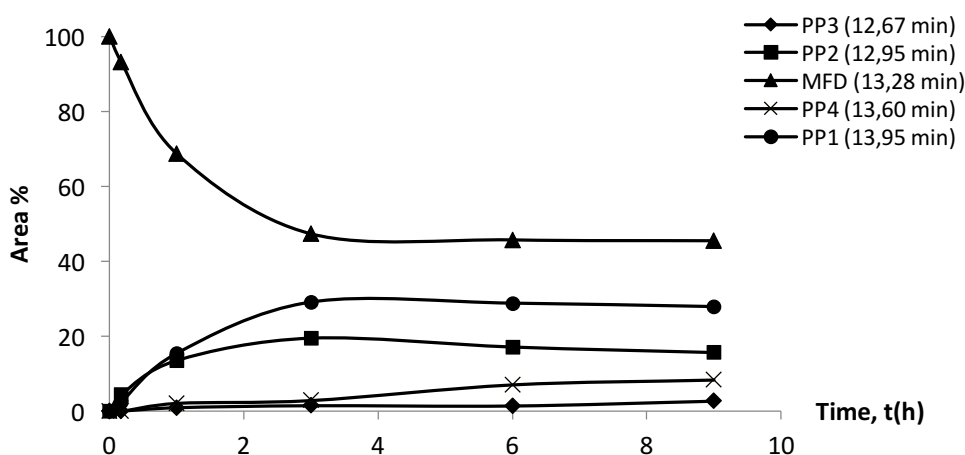


Figure 6: Change in amounts of parent MFD and degradation products as a function of time under photolysis at pH 4.4

Studies on the kinetics of these photoproducts showed that the decrease in amount of the parent compound MFD was related to the simultaneous appearance of two photoproducts PP1 at m/z 356 (two possible forms) and PP2 at m/z 344 (two possible forms) at irradiation time 0.17h. The two photoproducts PP1 and PP2 show their maximum intensities on after 3h of irradiation after which they also began to degrade into metabolites PP3 at m/z

330 (two possible structures) and PP4 at m/z 316, respectively. The structures of the four photo metabolites were all derived from the parent compound mefenpyr-diethyl. These structures indicate that the photoproducts (PP3) and (PP4) are formed by the loss of one terminal ethyl groups (mono-deesterification) of photoproducts (PP1) and (PP2) which are obtained from compound parent by dealkylation (concerted attacks of H and OH radicals on one of the terminal methyl groups) and mono-deesterification (of the free ester attached to the pyrazole ring), respectively. It is interesting to note that the both chemicals forms of photoproducts PP1, PP2 and PP3 have the same retention time and mass spectrum. The separation is not possible by our analytical conditions. These data confirm the result of Chnirheb et al. [2,3,15]. We can thus clearly see that the photolysis products P1 and P2 are a transient species which are not stable during the photolysis experiment, confirm the result of Chnirheb et al. [2,3,15].

Conclusion

Under sunlight, notable photodegradation of mefenpyr-diethyl was observed at pH 4.4. The kinetics of photolysis was determined to be first-order. From the GC/MS study on the photolysis, four photoproducts were identified. PP1 and PP2 have been identified as the major products of the photolysis of mefenpyr-diethyl. The mechanism of photodegradation under sunlight of this pesticide included alkylation and mono-desertification.

From this study, products PP1 and PP2 are a transient species, which are not stable during the photolysis experiment and are transformed into PP3 and PP4. Because of their current usage in many crops, photolysis will be important factors in determining its environmental fate in aquatic systems or in soil environment.

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