

Kinetics and Thermodynamic Photodegradation of the Insecticide Fenitrothion from Water

^{1,2}Sherif H. Abd-Alrahman, ³Z.H. Zidan, ³M.I. Abdel-Megeed,

²Monir M. Almaz and ¹Sobhy M. Yakout

¹Department of Biochemistry, College of Science, King Saud University,
P.O. Box, 2455, 11451 Riyadh, Saudi Arabia

²Department of Pesticides Residue and Environmental Pollution,
Central Agricultural Pesticide Laboratory, Agricultural Research Center, 12618 Giza, Egypt

³Department of Plant Protection, Faculty of Agriculture,
Ain Shams University, Kalubia, Egypt

Abstract: In order to study organophosphorus pesticides dissipation rates under abiotic conditions, researchers showed laboratory observations on the fenitrothion photodegradation and its temperature dependence. The kinetics and thermodynamic of fenitrothion were studied at temperature range 20-50°C under the irradiation of ultraviolet light. The results showed that photochemical reaction of fenitrothion in organic solvents such as acetone under UV light could be well described by the first kinetic equation and the photodegradation efficiency increases with increasing temperature in the range 20-50°C. The photodegradation rate constant of fenitrothion were 0.01, 0.03, 0.08 and 0.38 h⁻¹ and the corresponding half-lives were 31.6, 29.4, 9.6 and 7.8 h at 20, 30, 40, 50°C, respectively. The apparent activation energy was calculated to be 10.9 kJ mol⁻¹. Thermodynamic parameters of activation were also assessed for the degradation process.

Key words: Thermodynamic, photodegradation, insecticide, fenitrothion, UV light

INTRODUCTION

The Organophosphorus Pesticides (OPs) are an important group of pesticides used extensively all over the world for >60 years. They have been widely used as an alternative to organochlorine compounds for pest control. About 100 Ops account for w38% of the total pesticide usage. Organophosphorus insecticides represent >80% of total insecticides used in Egypt (Badawy, 1998).

However, most of them are highly toxic can exhibit chemical stability and resistance to biodegradation (Chiron and Barcelo, 1993), due to the probability of their being discharged into aquatic systems, great attention has to be paid to their degradation, to diminish their harmful effects on the environment. The principal degradation pathway for these pesticides involves photolysis, hydrolysis, dehalogenation and oxidation. Photochemical degradation is one of the major transformation processes and one of the factor controlling the fate of pesticides and other chemicals in the environment (Herrmann *et al.*, 1999).

Fenitrothion (O,O-dimethyl-(3-methyl-4-nitro phenyl) phosphorothioate, an organophosphorus pesticide) is

mainly used against spruce bud worms and cotton pests. It is widely used in tropical countries against malaria. Fenitrothion shows low toxicity against mammals (Nishizawa *et al.*, 1961). It is one of the most representative and commonly used organophosphorus pesticides (Derbalah *et al.*, 2004). Production of fenitrothion is estimated around 15,000-20,000 tones/year (IPCS). It is marketed under different trade names, e.g., Sumthion, Novathion and Metathion. It is considered to be a common river water pollutant and its residues in natural water undergo photodegradation, resulting in the release of many toxic metabolites, some being more toxic than the parent compound to aquatic organisms (Amoros *et al.*, 2000; Amoroso *et al.*, 2000; Derbalah *et al.*, 2004).

In Egypt, fenitrothion is used on cotton and other plants. Cotton receives, other than fenitrothion, insecticides such as carbaryl and deltamethrin so the soil under the plant usually contain a mixture of the used insecticides. Therefore, researchers found it important to investigate the stability of fenitrothion in aqueous solution (Zayed and Mahdy, 2008).

A variety of effective treatment methods have been reported for the degradation of fenitrothion, e.g., photolysis (Durand *et al.*, 1994; Lacorte and Barcelo, 1994), photocatalysis (Kerzhentsev *et al.*, 1996; Kormali *et al.*, 2004; Topalov *et al.*, 2003) and photo Fenton (Derbalah *et al.*, 2004) processes. Among these methods, photolysis one is highly promising because it can operate at ambient temperature and pressure with low energy photons does not require expensive catalyst and utilizes natural sunlight. An enormous literature is documented regarding photodegradation of organic pollutants. Very few studies have been published which consider the thermodynamic aspect of photodegradation. However, the quantitative data on thermodynamic parameters relating the degradation process is inadequate. To the best of the knowledge, there is lack of kinetic data which relates thermodynamic parameters of activation with photodegradation of pesticides.

The present research investigates the decomposition of fenitrothion by Ultraviolet (UV) under different temperature. The kinetics and thermodynamic of photolysis were studied.

MATERIALS AND METHODS

Fenitrothion certified analytical standard (purity 98%) was purchased from Dr. Ehrenstorfer GmbH, general structure of fenitrothion (Fig. 1). All organic solvent were HPLC grade and supplied by Merck Ltd. Deionized water was prepared by a Milli-Q water purification system. Anhydrous magnesium sulfate and Sodium chloride were of analytical grade and purchased from Merck Ltd. Anhydrous magnesium sulfate was activated by heating at 150°C for 4 h in the oven before use and kept in desiccators.

The stock solution of fenitrothion was prepared by dissolving 50 mg of the analyte (accurate weight) in 50 mL n-hexane to obtain concentration 1 mg mL⁻¹. Working standard solutions of 0.05, 0.1, 0.25, 0.5 and 1.0 µg mL⁻¹ were prepared by appropriately diluting the stock solution with n-hexane. Stock solution was stored at -20±2°C and working standard solutions were stored in ≤4°C when not in use. Calibration curves were generated by plotting peak area versus concentration.

Aliquots of fenitrothion stock solution (10 mg mL⁻¹ acetone) were placed in 100 mL pyrex flasks and completed to 100 mL with deionized water then exposed to Ultra Violet rays (UV-rays) at wave length 254 nm. Samples were taken at zero time and intervals 3, 6, 12, 24 and 48 h. Fenitrothion was extracted from water samples according method validated by Li *et al.* (2010). To

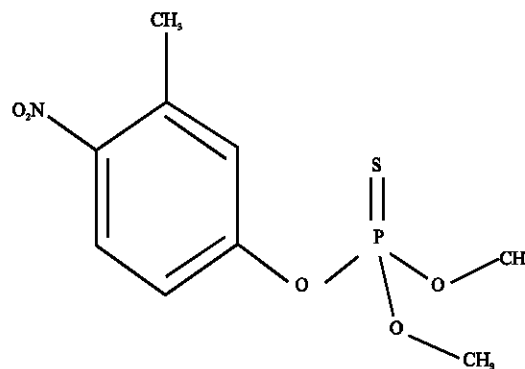


Fig. 1: Fenitrothian

determine the thermodynamic parameters of fenitrothion photo degradation this experiment was done under different temperatures 20, 30, 40 and 50°C.

Agilent 6890 (USA) Gas Chromatography Coupled with Nitrogen Phosphorus Detector (GC-NPD) was used for determination of butachlor residues. Capillary column HP-5 (30 m×0.25 mm×0.25 µm) was used for separation. Nitrogen was used as the carrier gas at a flow rate 2 mL min⁻¹. The following temperature program was employed: initial temperature of 180°C held for 1 min; increased at 25°C min⁻¹ to 220, held for 2 min yet another increase at 3°C min⁻¹ to reach 245°C. The injector temperature was 220°C. The injection volume was 1 µL for all standard and samples. Data analysis was performed using chemistation software.

RESULTS AND DISCUSSION

To evaluate the fate of pesticides in the environment the influence of both abiotic and biotic factors should be taken into account. Among the abiotic chemical factors affecting the behavior of pesticide, photochemical reactions are important. In the surface layers of aquatic system, photochemical reaction can play a dominant role in the conversion and degradation of pesticides. Figure 1 showed the time profile of fenitrothion photodegradation under different temperature. The temperature chosen represent Egyptian local conditions which are almost tropical (or subtropical) where the temperature reaches 45±5 in Summer. The results clearly showed that fenitrothion degradation varied according to time of exposure. The degradation increased as time increases. The degradation magnitude is proportional to the temperature. As the temperature increased the curve shape changes. Much sharper curves were obtained at higher temperatures. The degradation was faster at 50°C where fenitrothion concentration reach <5 µg mL⁻¹ in about 10 h. The degradation at 40°C was slower that

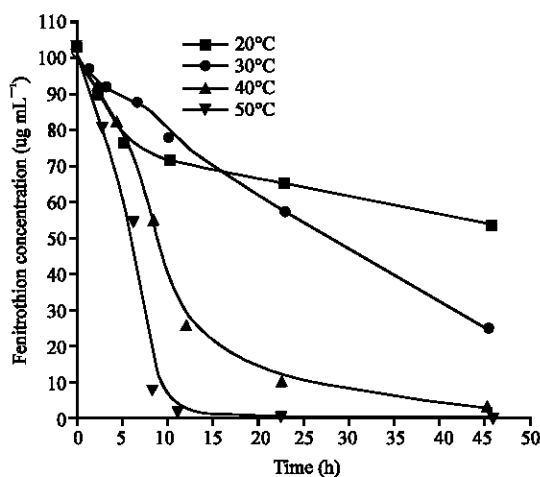


Fig. 2: Photodecomposition of fenitrothion by UV at 254 nm at different temperature

taking place in 50°C. The curve at 20 and 30°C are very slow and not reach to steady state in the studied time. Figure 2 show percent decomposition of fenitrothion at different temperature. Percentage was increased gradually with the exposure time and reached 2.4, 7.6, 13.2, 24.2, 34.7 and 54.5% after 1, 3, 6, 6, 12, 24 and 48 h exposure, respectively at 20°C. These results are in accordance to great extent with those obtained by Hegazy who studied the influence of acetophenone, benzoin, benzyl, nitrophenol and chlorophyll on the rate of photodegradation of the active ingredients pirimiphos-methyl, fenitrothion, malathion and prothiofos insecticides which are widely used in Egypt to protect vegetable crops from economic pests. Their results indicated that the benxion and benzyl compounds were found to be active as photosensitizers for all the studied insecticides. Chlorophyll and acetophenone generally showed no photosensitizing effects. A photostabilizing effect was clearly evident for acetophenone with prothiofos insecticides irradiated by UV-light (Yoshichika *et al.*, 2001), assessed the photodegradation extent of the organophosphorus pesticides, fenthion and disulfoton in the environment, degradation rates of their chemicals under irradiation by visible light Ultraviolet (UV) sources. Although, visible light did not cause photodegradation of either fenthion or disulfoton even after the maximal irradiation of 8 h. The photolysis rates of fenthion under UV irradiation in were higher than the degradation rates of disulfoton. This confirms that fenthion is more rapidly degraded than disulfoton.

To establish the photodegradation kinetics of fenitrothion, the effect of UV light exposure time (254 nm) on analytical response has been studied. For these studies a water solution containing 0.1 mg mL⁻¹ of

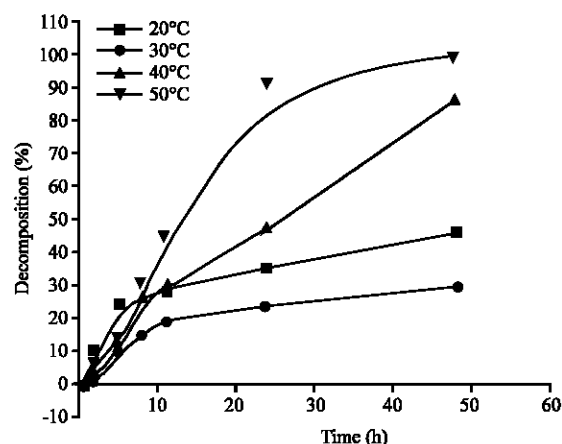


Fig. 3: Decomposition of percentage of fenitrothion by UV 254 nm at different temperature

Table 1: Rate constants and half-lives of fenitrothion photodegradation under different temperatures

Parameters	20°C	30°C	40°C	50°C
K h ⁻¹	0.0112	0.0297	0.0781	0.3848
R	0.9200	0.9900	0.9700	0.9800
t _{0.5} h	31.5600	29.3600	9.6200	7.7500

fenitrothion was exposed to UV irradiation for 0-48 h, subsequently, analyses were performed. From engineering point of view, it is useful to find out a simple user-friendly rate equation that fits the experimental rate data. According to many researchers the photocatalytic degradation of organic pollutants is described by pseudo-first order kinetics (Bhatkhande *et al.*, 2004; Cordero *et al.*, 2007; Evgenidou *et al.*, 2007). Pseudo first-order kinetic behavior was demonstrated by plotting the neperian logarithm of the percentage of undegraded compound against irradiation time (Fig. 3) according to the equation:

$$C_t = C_o \cdot e^{-kt}$$

Where:

C_t = Fenitrothion concentration (µg mL⁻¹) at time t (min)

C_o = Initial concentration (µg mL⁻¹)

k = Rate constant (h⁻¹)

The resulting first order rate constants have been used to calculate degradation rate for fenitrothion and thermodynamic parameters of activation. The required time for a response from the 50% of the initial concentration of reactants was calculated from the equation:

$$t_{0.5} = \frac{\ln 2}{k}$$

The kinetic parameters of fenitrothion are shown in Table 1 and Fig. 3 where the apparent rate constants and

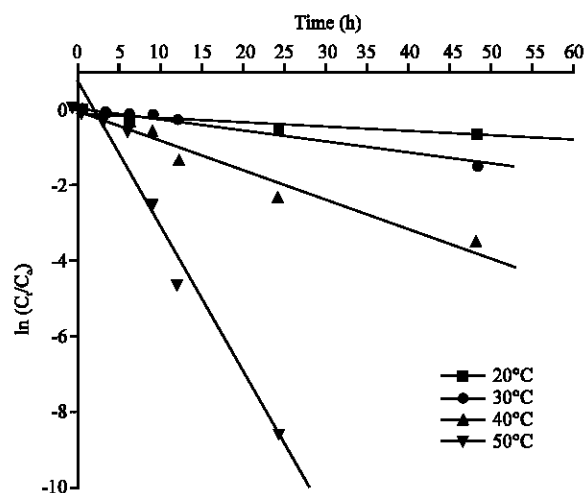


Fig. 4: Kinetics of fenitrothion pesticides

half-lives listed. In all cases, the kinetics of dissipation (Fig. 4) are followed an apparent first-order degradation curve with correlation coefficient R ranging from 0.92-0.999. The photolytic behavior of fenitrothion appeared strongly dependent on the temperature. In fact, the photolysis rate of fenitrothion was highly at higher temperature compared to photodegradation rat room temperature. The rat constant at 50°C was 40 times greater than the rat constant at room temperature. Increasing temperature reduce the halve-live of fenitrothion photo degradation. Half-lives ($t_{1/2}$) were 62, 23, 8.8 and 1.8 h at 20, 30, 40, 50°C, respectively (Table 1). It highly decreases with increasing temperature. The degradation rate increased with increase in temperature (Fig. 4) which was probably a consequence of an increased frequency of molecular collisions in the solution.

This influence of the temperature must be considered in the kinetic analysis of photodegradation processes carried out in a wide range of temperatures. The apparent rate constant and temperature can be expressed by arrhenius relation as follows:

$$k = Ae^{\frac{-E_a}{RT}}$$

Where:

- k = Apparent rate constant
- A = Frequency factor or preexponential factor
- E_a = Activation energy of the reaction
- R = General gas constant
- T = Absolute temperature

Translation of earlier equation resulted in:

$$\ln k_{app} = \ln A - \frac{E_a}{RT}$$

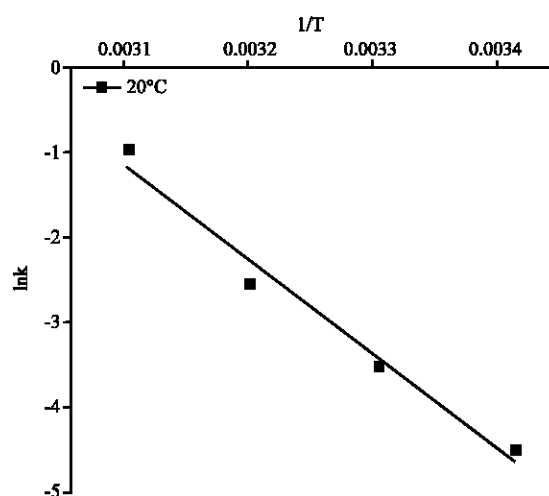


Fig. 5: Arrhenius plot on $\ln k$ against $1/T$ of fenitrothian photodegradation

Table 2: Thermodynamic parameters of fenitrothion photodegradation

Temperature (°C)	E_a (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
20	10.9	10.9	8.4	29.0
30	-	8.8	-	27.7
40	-	6.6	-	26.6
50	-	2.6	-	25.5

A linear plot of $\ln k_{app}$ versus $1/T$ yielded a straight line (Fig. 5) from which the activation energy can be obtained and are given in Table 2. The augmentation of the photodegradation activity is probably due to the increasing collision frequency of molecules in the solution. The other thermodynamic parameters for instance free energy of activation (ΔG), enthalpy of activation (ΔH) and entropy of activation (ΔS) were calculated (Table 2) using activation energy and apparent rate constant as follows:

$$\Delta G = -RT \ln k_{app}$$

$$\Delta H = E_a - RT$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The overall apparent activation energy to be 10.9 kJ mol⁻¹. This value is in good agreement with results reported in the literature (Herrmann, 2005; Lair *et al.*, 2008; Natarajan *et al.*, 1993; Soji *et al.*, 2009), quoting the values of the overall apparent activation energy of photocatalytic oxidation of different substrates in the range from 5.5-28.4 kJ mol⁻¹. These results are in agreement with the finding of Hegazy who studied the

influence of different temperature short ultraviolet and direct sunlight on the rates of the decomposition of diazinon and pirimiphos-methyl insecticide. The results indicated that the diazinon was less stable than pirimiphos-methyl when exposed to UV-rays after 3 h from application. The rate of degradation of the two tested insecticides varied according to their chemical structure, time of exposure and the wave length of UV-rays used.

CONCLUSION

In the knowledge, this is the first study to examine thermodynamic photodegradation of the insecticide fenitrothion in water. The results provide evidence that the use of UV irradiation under increasing environmental temperature can significantly increase the pesticide degradation. The effect of temperature from 20-50°C showed that the apparent rate constants follow the arrhenius relation. The activation energies of the degradation of phenolic rings were found to be 9.7-21.44 kJ mol⁻¹.

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