Stability of Photolysis and Hydrolysis of Prallethrin

Tiebing LIU*, Baojian LIU & Jie CHEN
University of Science and Technology, Hangzhou, China
Zhicheng YANG*, Chengyan ZHANG & Mingya XU
Hangzhou City Center of the Cereals and Oils Inspection Supervise Station, Hangzhou, China
**Corresponding author, The author should be considered co-first authors*

ABSTRACT: The photolysis and hydrolysis of prallethrin was studied in the laboratory. The result of the test showed that the photolysis reaction of prallethrin in aqueous solutions irradiated by 500w xenon lamp fitted to the first order dynamic equation. The results also showed that the hydrolysis rate of prallethrin in buffer solutions with pH values of 5 in 25°C were very slow. The rising temperature and pH values could both accelearate the hyrolysis. And discussion was also conducted to the mechanism of hydrolysis.
KEYWORD: Prallethrin; Photolysis; Hydrolysis; Gas Chromatography

Since the early 1980s, pyrethroids have been widely used in farm products, and it has become one of the main pesticides to control the pests and diseases. Pralethrin is the main effective constituent of a household aerosol insecticide commonly used in recent years. Photochemical degradation and hydrolysis are the major ways of its degradation. With the development of pest resistance to insecticide and increase numbers of pests controlling objects, there have been a lot reports on the photolysis and hydrolysis of pyrethroid insecticides [1-5]. However, there are relatively fewer reports on the stability of photolysis and hydrolysis of prallethrin insecticide. In the paper, the photolysis speed of prallethrin was studied under the light treatment with xenon lamp, and the hydrolysis dynamics of prallethrin were analyzed in the buffer solutions of different pH values and aqueous solutions of different temperature, with the aim to find out the stability of prllethrin pesticide in water environment so as to provide scientific basis for its scientific application.

1 MATERIALS AND METHODS

1.1 *Materials*

Pesticide: prallethrin (95%) pesticide was provided by the Yangzhou Pesticide Factory.

Reagents: redistilled petroleum ether (40-50 degrees C), anhydrous sodium sulfate, potassium biphthalate, sodium hydroxide, boric acid, potassium chloride, potassium dihydrogen phosphate were all analytically pure.

1.2 *The methods in experiment*

1.2.1 *Preparation of pesticides standard solution*

First, 0.0107g of standard substance was accurately weighed and put into the 50 mL volumetric flask, and than was dissolved by petroleum ether and set the constant volume to the scale, obtaining 214 mg/L of prallethrin standard stock solution.

1.2.2 *Preparation of different buffer solutions*

Clark-Lubs buffer solution[6] was used in this study.

1.2.3 *Hydrolysis test*

Firstly, prallethrin solution was added to the 250 mL test bottles with glass stopper, respectively, which were then dried using nitrogen. Then 200 mL of the buffer solution with different pH values were added to the bottles, and after fully mixed by shaking, the stoppers were plugged closely to the bottles. And then the bottles were placed in the incubator of 25°C ± 1°C, 50°C± 1°C. Starting from 0 am, 10 mL of water sample was taken from the reagent bottle each time at different time according to different kinds of pesticides for later use.

All the buffer solutions and containers for test use were all treated with dry heat sterilization. After sterilization, the pH of all solutions needed to be readjusted, and any oxidation needed to be avoided throughout the whole test.

1.2.4 *Photolysis test*

The photodegradation test was carried out in the NDC photochemical reactor. The 500W xenon lamp was used as the light source, and quartz cold well was used to surround the lamp, which could run through the condensed water to keep the stability of the temperature inside the reactor. The photolysis reaction tube was quartz tube, which was 70 mm away from the light source, and the light intensity was 1.05×10^{4} Lux. Water samples were taken regularly during the test to determine the changes of the pesticide concentration. During the photolysis test period, any other light resources should be isolated from the photolysis to reduce the influences on the test results.

The spectral signature of the xenon lamp used in the test was similar to that of the sunlight (Fig.1), which could ensure that the artificial simulated light degradation conditions were as close to the natural conditions as possible.

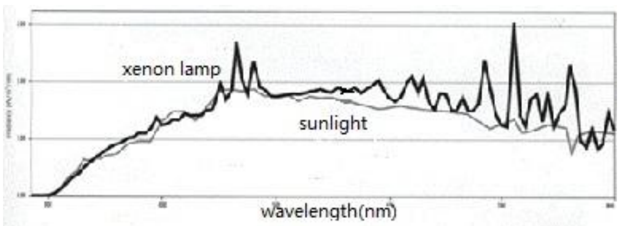

Fig. 1 The comparison between spectra of xenon lamp and spectra of the sunlight

1.2.5 *Analysis of pesticide residues*

Water extraction: 10mL of water sample was taken and put in the separatory funnel, which was added with 20mL×2 petroleum ether, and after organic phase combination, the rotary evaporator was used to evaporate and concentrate the sample into a certain volume for gas chromatography.

The recovery rate of pyrethroids at different pH buffer solutions was 93.4 - 100%, which showed a 3.03-10% deviation to the standard.

Conditions of determination by gas chromatogra - phy were as follows:

Shimadzu GC-14B gas chromatograph and electron capture detector were used for the gas chromatography.

Chromatographic column: the fused silica capillary column with 5% phenyl methyl silicone as the stationary phase and HP-5 length of 30m, diameter of 0.25mm and film thickness of 0.25μm.

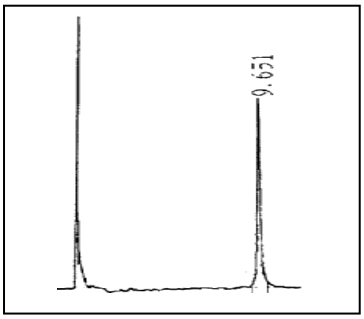

Fig. 2 GC

Temperature conditions: column temperature of 220°C, vaporizing chamber of 250°C, detecting chamber of 250 °C. Gas flow rate: nitrogen of 40mL/min.

Sample size: 1μL. The concentration of pralle - thrin standard solution: 25μg/mL, as Figure 2 shows.

2 RESULTS AND DISCUSSION

2.1 *Hydrolysis characteristics prallethrin*

The hydrolysis rate of pesticide was subjected to the influence of pesticide properties and water environment conditions, and the hydrolysis of pesticide in buffer solution system was fitted to the first order dynamic equation, which could be expressed using the following formula:

$$K = (\ln C_0 - \ln C_t)/t$$

$$T_{0.5} = \ln 2/K$$

Where, K is the hydrolysis rate constant; t is the reaction time; C_0 is the initial concentration; C_t is the pesticide concentration at t time.

The test results of the tested pesticides at different temperature and different pH conditions as well as the hydrolysis rate constant, hydrolysis half-life period and other values obtained from the above formula were as shown in Table 1 and Fig. 3.

Table 1 The hydrolysis of prallethrin in water solution

Pesticide	pH	T(°C)	n	K	$t_{0.5}$(d)	R
Prallethin	5	25	5	4.10×10^{-3}	169	-0.983
	5	50	6	4.80×10^{-3}	144	-0.943
	7	25	6	4.80×10^{-3}	144	-0.986
	7	50	8	6.72×10^{-2}	10.3	-0.991
	9	25	6	2.87×10^{-1}	2.46	-0.995
	9	50	6	2.88×10^{-1}	2.41	-0.994

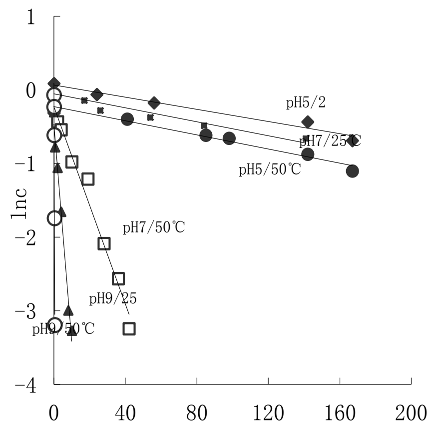

Fig. 3 The hydrolysis curve of prallethrin

The hydrolysis rate of the tested pesticide was subjected to the influence of pH. At the same pH conditions, the temperature of the solution also showed significant influence on the hydrolysis rate of the pesticide.

According to the Arrhenius empirical formula, lgk was used to map 1/T, and the activation energy of prallethrin hydrolysis was calculated according to the straight slope (Table 2).

Table 2 The activation energy of prallethrin products under different pH conditions

Pesticide	pH	Ea（kJ/mol）
prallethin	5	5.05
	7	84.5
	9	101

Activation energy could reflect the difficulty level for the reagent molecule to carry out reaction. Under the same conditions, the smaller the needed activation energy is, the easier the molecule to carry out the chemical reaction is. The results showed that with the increase of pH, the activation energy also increased, indicating that at high pH, hydrolysis became more and more sensitive to temperature.

2.2 *Discussion on the mechanism of hydrolysis reaction*

According to the mechanism of the alkaline hydrolysis of esters, in allethrin molecules, due to the polarization of carbonyl, the carbonyl carbon atom carried with a partial positive charge, which would be first attacked by the hydroxyl ion which was served as the affine reagent, and then formed the unstable negative ion. Due to the combination of the hydroxyl ion and carbonyl carbon atom, the migration of the electron cloud from the oxygen atom to the carbonyl carbon atom in the acyl oxygen bond resulted in the carbon oxygen bond cleavage in the carbonyl. As shown in Fig.4.

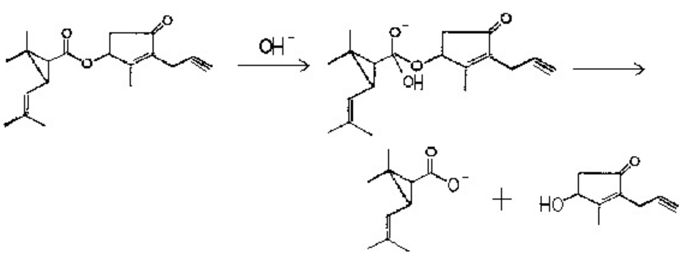

Fig.4 The hydrolysis degradation mechanism of prallethrin

Prallethrin was stable in acid aqueous solution, but with the increase of the concentration of OH^- in water environment, the hydrolysis intensified. The hydrolysis rate presented positive temperature effect, that is, the hydrolysis rate increased with the increase of water temperature. The above reaction process showed that the hydrolysis reactions of the 3 kinds of tested pesticides were all nucleophilic reaction. With the increase of the NaOH concen - tration, the concentration of OH^-, as the nucleophilic reagent, also increased, and thus speeding up the reaction rate.

In acidic condition, H^+ could protonize the carbonyl, and as the nucleophilic reagent, H_2O would attack carbonyl, which could increase the acidity. With the increase of H^+ concentration, H_2O began to exist in the form of H_3O^+, and thus the nucleophilicity decreased and the reaction speed became slow down. The final destination and effect of these kinds of compounds after entering the water system is still a problem worthy of attention.

2.3 *Photolysis character of prallethrin*

Prallethrin had 4 sensitive points, 3 double bonds and cyclopropane rings. The double bonds could be epoxidized, or transformed into cyclopropane ring in the existence of allyl. The acid part of cyclopropane ring could be isomerized through the intermediate of bivalent radical. The test determined the photo-chemical degradation of prallethrin in the aqueous solution under the 500W xenon lamp, and the results were shown in Table 3 and Fig.5.

Table 3 The photolysis of prallethrin in water

No	Time of Light(h)	C.P.*（mg/L）
1	0.0	0.552
2	0.25	0.394
3	0.50	0.336
4	1.00	0.209
5	1.50	0.144
6	2.00	0.099
7	3.00	0.049
8	4.00	0.020

* The concentration of the pesticides

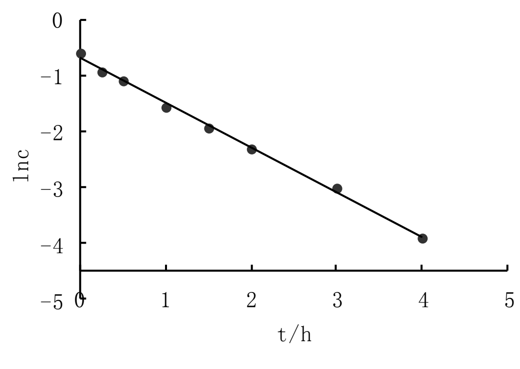

Fig. 5 The photolysis curve of prallethrin

The results showed that: after light treatment, prallethrin showed significant changes in concen-tration, and at the light intensity of 1.05×10^4Lux, the hydrolysis of this pesticide in water phase was fitted to the first order dynamic equation with the photolysis half-life period of 0.87 h. Generally speaking, the indoor light intensity was about 100 - 4000 Lux, and therefore when it was used as the indoor hygiene medication, it should keep the air fully circulate from indoor to outdoor after using it as the liquid for some time to reduce the possible harm to human health.

REFERENCES

[1] Hua RM, Yue YD, Tang F. 1995, The photosensitive effects of parathion-methryl on the photode-gradation of three pyrethroid insecticides. *Environmental Chemistry*, (14): 508-512.

[2] Yue Yd. 1991, The effects of several pesticides on the photodegradation of pyrethroid insecticides. The Collected Papers of First National Seminar for the Youth Scientific and Technical Workers of Plant Protection. *Beijing: Science and Technology of China Press*, 450-455.

[3] James R M. 1990, Chemical and photochemical isomerization of deltamethrin. *Journal of Agricultural and Food Chemistry*, 38:1613-1617.

[4] Ruzo L O. 1983, Involvement of oxygen in the photoreactions of cypermethrin and other halogenated pyrethroids. *Journal of Agricultural and Food Chemisry*, 31: 1115-1117.

[5] Holmstead RL, Fullmer DG, Ruzo LO.1978, Pyrethroid photodecomposition: Pydrin. *Journal of Agricultural and Food Chemistry,* 26: 954-95.

[6] The Central People's Government of the People's Republic of China. 1990, *Guidelines for the testing of chemicals*, 113-115.