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Hydrolysis and Photodegradation of Trifloxystrobin in Aqueous Solution

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Hydrolysis of trifloxystrobin was investigated in pH 4-10 aqueous solutions at 25, 40 and 50 °C. Its photochemical experiments in acidic, neutral, alkaline solutions and 1-10 mg/L humic acid solutions were conducted. Trifloxystrobin hydrolytic rate was first-order with respect to hydroxide ion concentration. For each 10 temperature rising, the rate constant for hydrolysis increased 2-4 times. The photolytic $T_{1/2}$ of trifloxystrobin at pH 4, 7 and 9 was 13.0, 11.9 and 4.3 h, respectively. In the 1-10 mg/L humic acid solutions, the photodegradation rate constants corrected for light screening of trifloxystrbin were 0.0592-0.0577 h^{-1}, basically decreasing with the humic acid concentration increasing. It was concluded that in the aqueous solution, the key nucleophilic reaction partner was hydroxyl ions. Raise of temperature could accerlate hydrolysis of trifloxystrobin. The hydrolysis could accelerate the photolysis of trifloxystrobin and light screening had an effect on the photodegradation rate constants of trifloxystrobin.

Keywords: Trifloxystrobin, Hydrolysis, Photolysis.

INTRODUCTION

Trifloxystrobin{methyl-α-(methoxyimino)-2-[({1-[3-(trifluoromethyl)phenyl]ethylidene}amino)oxymethyl]benzeneacetate} (TFS) is a systemic broad-spectrum foliar fungicide marketed by Bayer Crop Science. TFS exhibits activity against many fungal pathogens such as *Ascomcete, Basidiomycete, Deuteromycete* and *Oomycete* classes. It has particular effect on anthracnose[1], downy mildew, powdery mildew[2], rice blast[3], rice shealth blight and false smut[4] attacking vegetable, fruit and grain crops. The compound can be used to control fungus in greenhouse, nursery, orchard, vegetable and paddy field crops. Although trifloxystrobin is considered to be less toxic to birds, mammals, bees, other beneficial insects and earthworms[5], it has been classified as highly toxic to Bufo cognatus tadpoles[6], *Oncorhynchus mykiss* trout and the marine crustacean *Mysidopsis bahia*[5]. Hence, aquatic organisms may be at risk of exposure to trifloxystrobin through spray drift, direct overspray, atmospheric transport, runoff and movement of animals through fields during application. Therefore, it was necessary to assess the degradation of trifloxystrobin in aqueous solution.

The primary degradation in aquatic systems is hydrolysis and photodegradation. Trifloxystrobin is the first strobilurin compound with an oximether side chain. As shown in Fig. 1, the chemical structure of trifloxystrobin can appear in four geometrical isomers of EE, EZ, ZE and ZZ based the connected group arrangement of the two N=C double bonds. Banerjee *et al.*[7,8] built the photoisomerization kinetics of trifloxystrobin in acetone and found it might convert to four geometricals isomers in artificial sunlight under laboratory conditions. The isomerization reached equilibrium after 7 h. They also isolated ZZ, EZ, ZE isomer crystalline form and reported the X-ray crystallographic structures of them[9-11]. Since trifloxystrobin is a kind of ester, it was susceptible to hydrolysis. The hydrolysis of four geometric isomers of trifloxystrobin with 0.05 mol/L NaOH resulted in four corresponding acid metabolites, namely TFS EE-, EZ-, ZE- and ZZ-acids, which were stable in aqueous solution[8].

In natural aquatic systems, there are a number of environmental factors such as temperature, pH values[12,13], TiO_2 [14,15] and humic substances[16,17] which can effect on hydrolysis and photodegradation of compounds in aqueous solution. In this study, the hydrolysis and photodegradation of trifloxy-strobin were conducted. The research paper presents the results of the investigations on the hydrolysis of trifloxystrobin in different temperature and pH values and the photolysis of trifloxystrobin as a function of pH and the presence of humic acid. In addition, the major products and mechanism of reaction are discussed. This work provides information and data to better understand environmental fate of trifloxystrobin and assess the risk of environmental contamination in the aqueous systems.

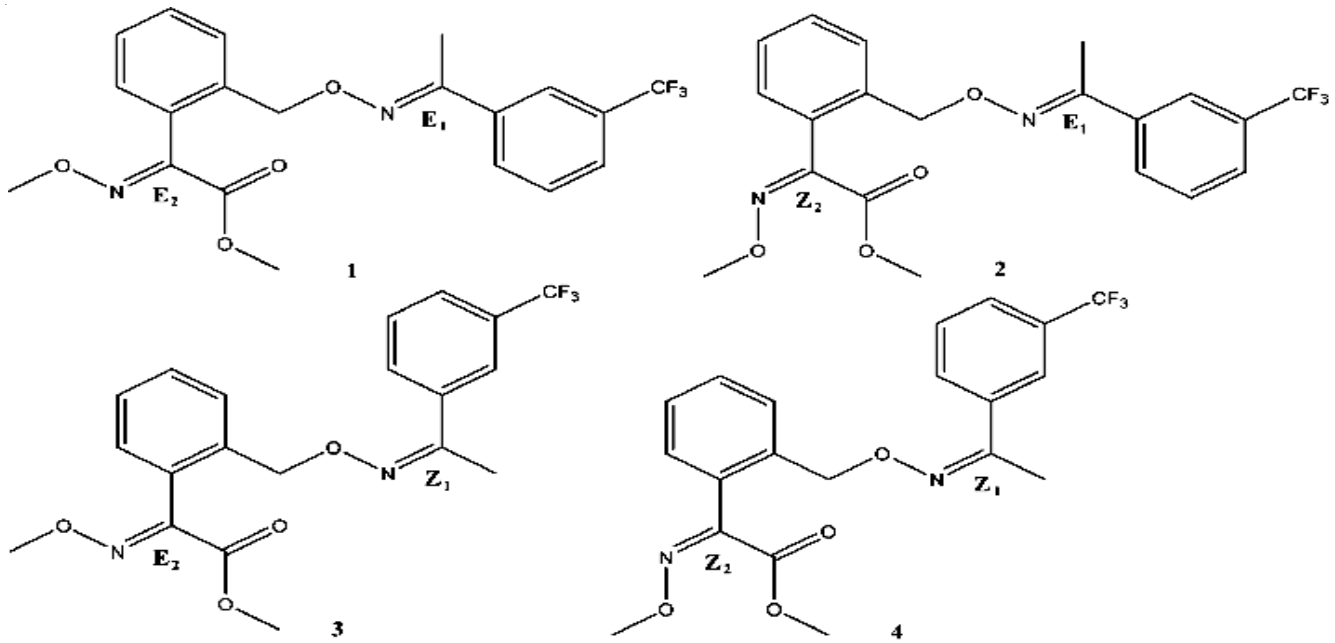

Fig. 1. Four geometric structure of trifloxystrobin

EXPERIMENTAL

Trifloxystrobin (purity = 99.7 %) was obtained from Jiangsu Changqing Agrochemical Co. Ltd. of China. Ethyl acetate used for the chromatographic analysis is HPLC-grade, purchased from Dikma Technologies Inc., Beijing, China. Sodium hydroxide, potassium hydrogen phthalate, potassium dihydrogen phosphate and boric acid used to prepare buffered solution are all analytical grade. Analytical grade acetonitrile, sodium chloride and anhydrous magnesium sulfate were used as extracting regents. All analytical grade regents were from Beijing Chemical Works, China. Humic Acid (HA) is chemical grade purchased from Guangfu Fine Chemical Research Institute, Tianjin, China.

Buffer solutions: Buffer solutions should be prepared using reagent grade chemicals and water. The pH values of buffer systems used in this study ranged from 4 to 10. The pH4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 buffer solutions were prepared by adding 0.4 mL 0.1 mol/L NaOH and 50 mL 0.1 mol/L $KHC_8H_4O_4$, 23.85 mL 0.1 mol/L NaOH and 50 mL 0.1 mol/L $KHC_8H_4O_4$, 5.7 mL 0.1 mol/L NaOH and 50 mL 0.1 mol/L K_2HPO_4, 29.63 mL 0.1 mol/L NaOH and 50 mL 0.1 mol/L K_2HPO_4, 46.8 mL 0.1 mol/L NaOH and 50 mL 0.1 mol/L K_2HPO_4, 21.3 mL 0.1 mol/L NaOH and 50 mL 0.1 mol/L HBO_3, 43.9 mL 0.1 mol/L NaOH and 50 mL 0.1 mol/L HBO_3 to 100 mL volumetric flasks respectively, then diluting to a constant volume of 100 mL with water. The pH value of each buffer solution should be checked with a calibrated pH meter to a precision of at least 0.1 at 20 °C.

Chromatographic method: Trifloxystrobin was analyzed by Agligent 7890A GC (Agilent Technologies, Ltd., USA) equipped with 5 % phenyl methyl siloxan column (30 m × 320 μm × 0.25 μm) and ECD detector. The gas chromatograph was operated in split/splitless injection mode with the split flow of 11.631 mL/min. The injector temperature was 280 °C and the injection volume was 1 μL. Nitrogen was used as carrier gas at a flow rate of 2 mL/min. The oven program was as follows: isothermal at 120 °C for 1 min, then heated from 120 to 240 °C at 30 °C min^{-1}, isothermal at 240 °C for another 1 min, followed by heating from 240 to 280 °C at 10 °C min^{-1}, finally isothermal at 280 °C for 5 min.

The sample was performed by HPLC and ESI-MS-MS (Agilent 1260-G6460B QQQ manufactured by Agilent Technologies Ltd., USA). The chromatographic separation was performed with 4.6 × 100 mm × 3.5 μm Agilent C18 column (Agilent Technologies Ltd., USA) using an acetonitrile/0.1 % formic acid solvent following a gradient (10 % acetonitrile over 5 min, from 10 % to 40 % acetonitrile from 5 to 7 min, from 40 to 60 % acetonitrile from 7 to 10 min, 60 % acetonitrile from 10 to 15 min, from 60 to 70 % acetonitrile from 15 to 25 min) for 25 min. The flow rate was 200 μL/min with an injection volume of 5 μL. ESI was performed in positive-ion mode with the parameters of 15 psi nebulizing gas (N_2) pressure, 3.5 kv capillary voltage, fragment 80 v voltage and collision energy of 7 v. The acquisition was from *m/z* 100 to *m/z* 450.

Hydrolysis in buffered solution: Ten samples of each buffered solution of trifloxystrobin at a concentration of half of the water-solubility 0.30 mg/L were placed in 25 mL measured flask at pH 4, 5, 6, 7, 8, 9 and 10 and temperatures of 25 ± 1 °C, 40 ± 1 and 50 ± 1 °C in the dark. The temperature was controlled with constant climate chamber. All samples were prepared in duplicate. In order to restrain the growth of bacteria, the measuring flasks and buffered solutions were sterilized in an autoclave at 121 °C for 0.5 h. The pH value of the buffer solutions was adjusted with 0.1 mol/L NaOH or 0.1 mol/L HCl prior to use. Each sample was removed at certain timed intervals and extracted with 40 mL ethyl acetate in ultrasonic water bath for 25 min. The extracted solution was evaporated to dryness, after which 1 mL aliquot of ethyl acetate and 1 mL acetonitrile were added into the tube to dissolve the sample which served as the sample for analyzing with GC and HPLC-MS-MS.

Photolysis in buffered solution and humic acid solution: Photochemical reactions were conducted using pH5, 7 and 9 buffered solutions and 1.0-10 mg/L humic acid solutions of trifloxystrobin in quartz test tubes with a merry-go round. Samples were irradiated with 5 W mercury lamp. The initial concentration of trifloxystrobin is 1.23×10^{-6} mol/L. Non-irradiated samples of trifloxystrobin were employed as dark controls.

RESULTS AND DISCUSSION

The hydrolysis of trifloxystrobin at pH 4 and pH 5 was minimal as no noticeable hydrolysis occurred at 50 °C 5 days later, which meaned the $T_{1/2}$ of trifloxystrobin at pH 4 and pH 5 are longer than 1 year. The hydrolysis of trifloxystrobin at pH 6, 7, 8, 9 and 10 at 25 °C, 40 and 50 °C were described by pseudo first order reaction kinetics. The observed pseudo-first order hydrolysis rate constants k and half-lives $T_{1/2}$ under various temperature and pH conditions were listed in Table-1. It was concluded from Table-1 that the hydrolytic rate of trifloxystrobin increased with the rising temperature at pH 6-10. The hydrolytic of trifloxystrobin increased with pH increasing at the same temperature.

The second-order reaction rate constant, k_{OH}, was determined from the slope between pH 6 and pH 10 in a plot of log k *vs*. pH according to the relationship.

$$k_{OH} = \frac{k}{[OH^-]} \quad (1)$$

It was shown in Fig. 2 that the lg k was linear correlation with pH between pH 6-10 at 25 °C, 40 and 50 °C and the slope of the line was approximately +1.

TABLE-1
HYDROLYTIC KINETIC PARAMETERS OF TRIFLOXYSTRBIN UNDER DIFFERENT TEMPERATURES AND pH VALUES

T (°C)	pH	k (h^{-1})	$T_{1/2}$ (h)	R^2
50	6	0.0009	770.1	0.9827
	7	0.0131	52.9	0.9781
	8	0.1028	6.7	0.9545
	9	0.5456	1.3	0.9934
	10	5.8932	0.1	0.9718
40	6	0.0004	1732.9	0.9724
	7	0.0063	110.0	0.9944
	8	0.0354	19.6	0.9551
	9	0.2336	3.0	0.9956
	10	2.7711	0.3	0.9578
25	6	0.0002	3465.7	0.9796
	7	0.0008	866.4	0.9853
	8	0.0191	36.3	0.9966
	9	0.0837	8.3	0.9813
	10	0.8294	0.8	0.9901

It indicated that hydrolytic rate of trifloxystrobin was positive correlation with hydroxide ion concentration and appeared to be base catalyzed. The second-order reaction rate constant for base hydrolysis, k_{OH}, calculated from eqn. 1 were 4.58×10^4, 1.42×10^5 and 3.31×10^5 at 25, 40 and 50 °C respectively.

The completely hydrolyzed solution was assayed *via* HPLC/MSMS shown in Fig. 3. The MS spectra indicated that there was only one hydrolytic product (α)-α-(methyoxyimino)-2-[[[[1-[3-(trifluromethyl)phenyl]ethylidene]amino]oxy]-methyl]benzene acetic acid (TFS-acid). The TFS-acid remained stable in alkaline solution and no further hydrolytic products were detected. It was concluded that TFS-acid was the only one main hydrolytic product and it was not easily to be decomposed.

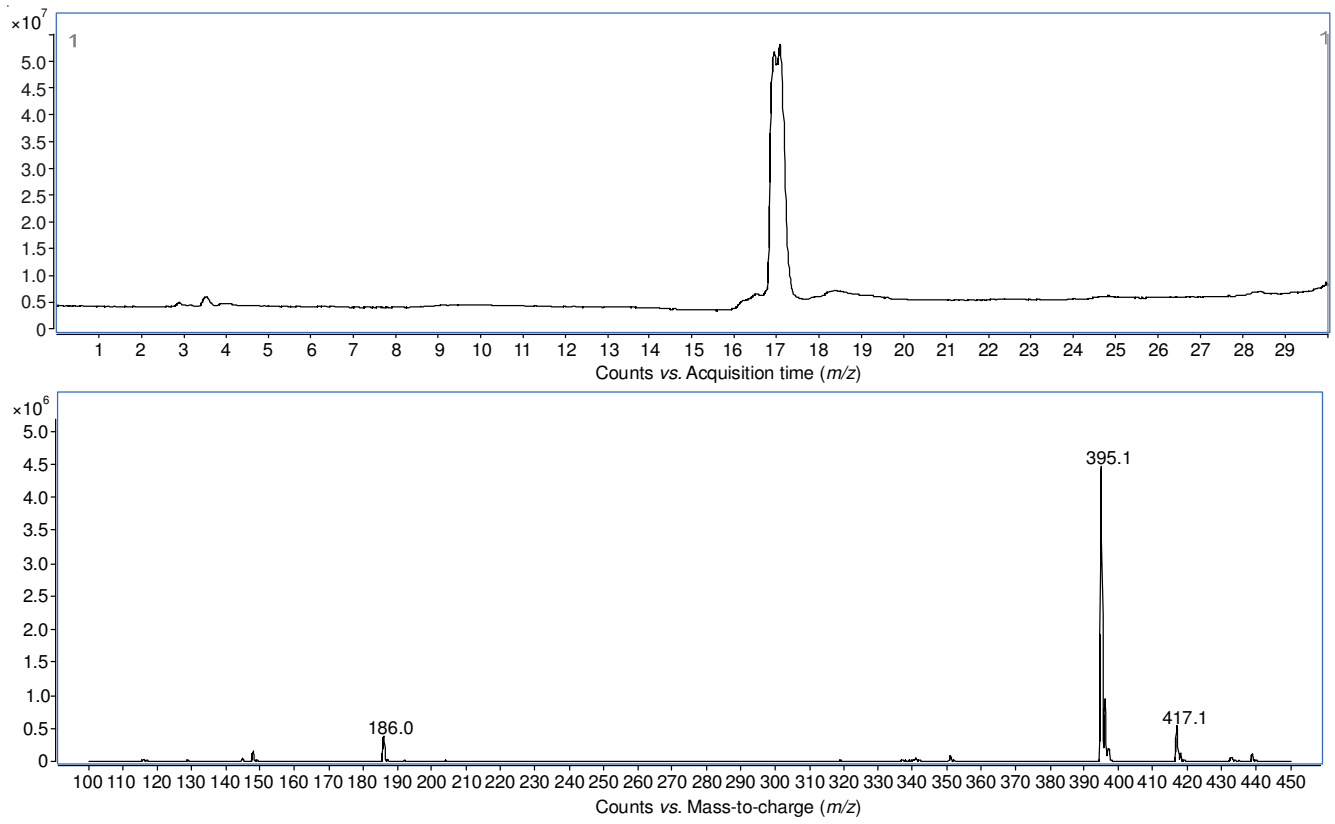

Fig. 3. HPLC-MS-MS spectrogram of trifloxystrobin hydrolysis

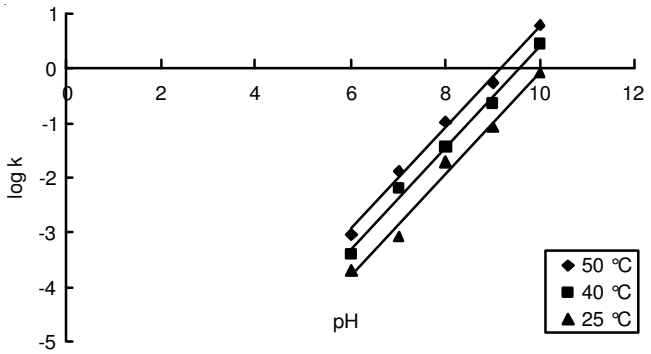

Fig. 2. Hydrolytic rate constant of trifloxystrobin at different temperatures and pH values

On the basis of Arrhenius equation, the activation parameters of the hydrolysis of trifloxystrobin at different pH values were calculated as Table-2. E_a was apparently the highest at pH 7 indicating that the hydrolysis of trifloxystrobin was the most sensitive to temperature variation at pH 7.

TABLE-2
ACTIVATION ENERGY AT DIFFERENT pH VALUES

pH values	6	7	8	9	10
E_a (KJ/mol)	47.0	95.7	51.8	62.4	62.6
ln A	10.4	31.5	16.8	22.6	25.1

Photolysis of trifloxystrobin in different pH buffers: The photolysis of trifloxystrobin at pH 4, 7 and 9 was described by pseudo first order reaction kinetics (Fig. 4) and the kinetic parameters were listed in Table-3. The photolytic $T_{1/2}$ of trifloxystrobin at pH 4, 7 and 9 was 13.0, 11.9 and 4.3 h respectively. The main photolysis pathway was isomerization of TFS (EE converted to ZZ, ZE and EZ) and no further degradation was observed when the isomerization process reached equilibrium during illumination at pH 4. In alkaline solutions, photolysis and hydrolysis appeared simultaneously. The four TFS geometric isomers transformed into the four corresponding acid. It was consistent with the hydrolytic results and the results of Banerjee *et al.*[7,8]. It is noted that the rate constant was greater than the sum of both hydrolysis and photolysis rate constants (Table-3), it indicated that it was impossible that hydrolysis and photolysis contribute independently to the decomposition of trifloxystrobin. It was concluded that the hydrolysis reduced the concentration of the four ester geometric isomers and he isomerization of TFS-EE was accelerated by this hydrolysis. Thus the photolysis rate constant was commonly greater in alkaline than in acidic system.

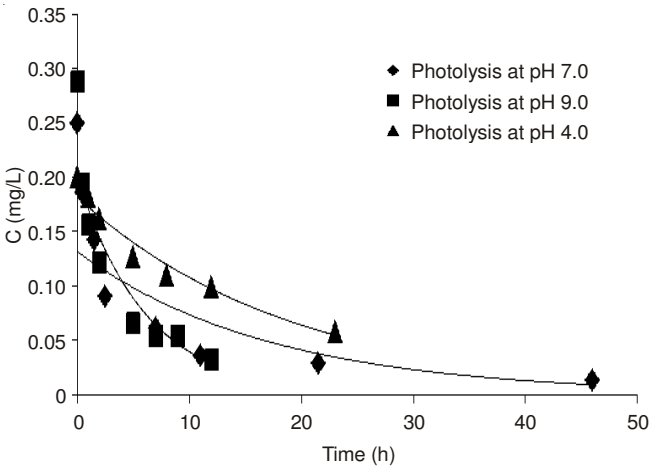

Fig. 4. Photolytic kinetics of trifloxystrobin at 25 °C

Table-3
PHOTOLYTIC KINETIC PARAMETERS OF TRIFLOXYSTRBIN UNDER DIFFERENT pH VALUES

pH values	kinetic eq.	R^2	k (h^{-1})	$T_{1/2}$ (h)
4	$\ln[C]/[C_0]=-0.0523t$	0.9708	0.0523	13.0
7	$\ln[C]/[C_0]=-0.0594t$	0.8135	0.0584	11.7
9	$\ln[C]/[C_0]=-0.1626t$	0.9182	0.1626	4.3

Photolysis of trifloxystrobin in humic acid solution: The concentration of humic acid in natural waters was between 1 and 10 mg/L[18]. The humic acid in water could absorb UV light and produces reactive oxygenated species such as single oxygen and hydroxyl which could cause the increasing of photo-degradation rates[19,20]. The light screening of humic acid could also cause the decreasing of photodegradtion rates[21,22]. The results of the effect of humic acid on the trifloxystrobin photodegradation rates were labeled as Table-3.

Fig. 5 gave the UV-visible spectra of several solutions. The spectra showed that the trifloxstrobin solution had the lowest absorbance at 200-400 nm and the absorbance of trifloxystrobin/humic acid solutions increased with the increasing concentration of humic acid.

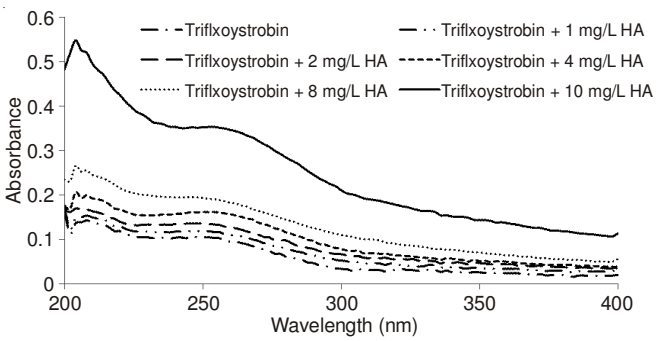

Fig. 5. UV-visible spectra of trifloxystrobin/humic acid (HA) solutions

A light-screening factor was introduced to analyze the effect on degradation rate constants due to this light screening. Make two assumptions and simplify the calculation of the light-screening factor as eqn.[23].

$$S(\lambda) = \frac{1 - 10^{-1.2\alpha(\lambda)z_{mix}}}{1.3 \times 1.2 z_{mix}\alpha(\lambda)} \quad (2)$$

where $S(\lambda)$ is the screening factor, z_{mix} is the vertical distance, $\alpha(\lambda)$ is the beam attenuation coefficient in cm^{-1} which can be obtained from the Beer-Lambert law[23].

$$A(\lambda) = [\alpha(\lambda) + \varepsilon_i(\lambda)C_i]l \quad (3)$$

where $A(\lambda)$ is the absorbance of the solution, $\varepsilon_i(\lambda)$ is the absorptivity of trifloxystrobin at particular wavelength in (mol/L)/cm, C_i is the concentration of trifloxystrobin of interest in moles per liter (mol/L) and l is the path length of the light in the solution commonly expressed in centimeters.

Given the lamps used have a narrow wavelength range and the samples were well-mixed and clear. The photodegradation rate constant in the presence of humic acid could be corrected by eqn. 4[13].

$$k_{corr} \approx k_{obs} / S(\lambda) \quad (4)$$

where k_{obs} is the experimental photodegradation rate constant for trifloxystrobin in the presence of humic acid in h^{-1}, k_{corr} is the photodegradation rate constants corrected for light screening. The photodegradation experimental rate constant of trifloxystrobin in buffer and humic acid solutions, the screening factor for given humic acid solutions and the photodegradtion rate constant corrected for light screening of trifloxystrobin in humic acid solutions were listed in Table-4.

TABLE-4
EXPERIMENTAL (k_{obs}) AND LIGHT SCREENING CORRECTED (k_{corr})PHOTODEGRADATION RATE CONSTANTS OF pH 7 TRIFLOXYSTROBIN/HUMIC ACID SOLUTIONS AT 254 nm

Solution	k_{obs} (h^{-1})	S(λ)	k_{corr} *h^{-1})
1.23×10^{-6} mol/L TFS	0.0594	-	-
1.23×10^{-6} mol/L TFS +1.0 mg/L HA	0.0583	0.980	0.0593
1.23×10^{-6} mol/L TFS +2 mg/L HA	0.0574	0.960	0.0597
1.23×10^{-6} mol/L TFS +4 mg/L HA	0.0548	0.925	0.0592
1.23×10^{-6} mol/L TFS +8 mg/L HA	0.0518	0.890	0.0582
1.23×10^{-6} mol/L TFS +10 mg/L HA	0.0417	0.723	0.0577

As Table-4 illustrated, in the addition of 1-10 mg/L humic acid to a pH 7 phosphate-buffered trifloxystrobin solution, the photodegradation rate constants corrected for light screening of trifloxystrbin decreased with the humic acid concentration increasing. It was concluded from the results that light screening has an effect on the photodegradation rate constants of trifloxystrobin in the humic acid solutions. It would also likely affect potodegradation of trifloxystrobin in natural water systems.

Conclusion

The hydrolysis of trifloxystrobin was investigated in aqueous buffer solution at different pH values and temperatures. The results indicated that the hydrolysis of trifloxystrobin was pH and temperature dependent. In the studied pH range of 6-10, trifloxystrobin hydrolytic rate was first-order with respect to hydroxide ion concentration which indicated only alkaline catalysis enabled the hydrolysis of trifloxystrobin. Rising temperature could also accelerate the hydrolysis of trifloxystrobin. For each 10 °C rising, the rate constant for hydrolysis increased 2-4 times. E_a was the highest at pH 7 which indicated that the hydrolysis of trifloxystrobin was the most sensitive to temperature at pH 7. TFS-acid was the only one main hydrolytic product in darkness.

The photochemical reactions were conducted in different pH buffered solutions and 1-10 mg/L humic acid solutions. The photolysis rate increased with the increasing of pH values which indicated that the hydrolysis could accelerate the photolysis of trifloxystrobin. In the 1-10 mg/L humic acid solutions, the photo-degradation rate constants corrected for light screening of trifloxystrbin decreased with the humic acid concentration increasing. Light screening had an effect on the photodegradation rate constants of trifloxystrobin in the humic acid solutions.

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