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Hydrolysis of Thiamethoxam

Z. Liqing,[1,2] L. Guoguang,[2] S. Dezhi,[1] Y. Kun[2]

[1] School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, 150090, People's Republic of China
[2] Henan Key Laboratory for Environmental Pollution Control, College of Chemistry and Environmental Science, Henan Normal University, Xinxiang, 453007, People's Republic of China

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The hydrolysis of pesticides is an area that has received extensive study, since most compounds entering the environment will at some stage be in contact with water or be adsorbed in lipophilic media. It is useful to understand hydrolysis pathways in order to determine the stability of the pesticide, to identify its hydrolytic products, and thus assess their toxicology, and to analyze residues.

Thiamethoxam belongs to a new class of insecticides known as neonictinoids. Its molar structure was shown in figure 1. Thiamethoxam is approved for use as soil, foliar, and seed treatment for the control of aphids, whiteflies, and some beetles among others (Maienfisch, et al., 2001). The U.S. EPA promulgated rules for thiamethoxam use beginning in 2000 (U.S. Environmental Protection Agency, 2000, U.S. Environmental Protection Agency, 2000, U.S. Environmental Protection Agency, 2001, U.S. Environmental Protection Agency, 2002). During 2001, thiamethoxam was approved for various uses by the Massachusetts Department of Food and Agriculture, the Canadian Pest Management Regulatory Agency, and the Australian National Registration Authority for Agricultural and Veterinary Chemicals. Thiamethoxam, imidacloprid, and other neonicotinoids are expected to replace organophosphates as the most widely used insecticides worldwide (Antunes-Kenyon, et al., 2001).

As for the environmental fate for neonictinoids, researches published focus on the fates of imidacloprid in environment. The photolysis (Wamhoff, 1999, Schoz, 1999, Shan et al., 1998, Shan et al., 1999, Wei, 2002, Malato, 2001) and hydrolysis of imidacloprid (Wei 2002, Malato, 2001, Phillip, 2004, Zheng, 1999) in environment , its migration and transformation in soil (Shan, 1998, 1999, Phillip, 2004, Zheng, 1999, Liu, 2001, Xuan, 2000, Rouchand , 1994, Barb 2000), and its effecting on soil respiration have been study. Few researches was done to investigate the environment of thiamethoxam (Barb, 2000).

Thiamethoxam has been introduced to Chinese markets, has the bright future in

Correspondence to: L. Guoguang

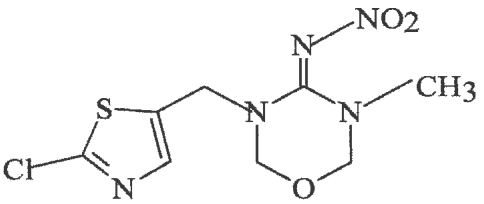

Figure 1. Molar structure of thiamthoxam.

market because of its high insecticidal effectiveness and low mammalian toxicity. The paper reports the effect of pHs and temperatures on the hydrolysis of the thiamethoxam and the hydrolytic mechanism of thiamethoxam.

MATERIALS AND METHODS

Thiamethoxam purchased from Pesticide center of Beijing is above 98% purity. Sodium hydroxide, potassium hydrogen phthalate, potassium dihydrogen phosphate, boric acid, which are all analytical grade, were used to prepare buffered solution. Redistilled dichloromethane is used as extracting reagent. The thiamethoxam was analyzed by HP1100 HPLC equipped with diode array detector, Zorbax-C18 column (250mm × 4.6mmID). The hydrolytic product was analyzed by Aglient6890/5973N GC-MS equipped with HP-5MS capillary column (30m x 0.25mm x 0.25μm. Water bath (Beijing Changfeng Equipment Company) was employed to maintain the temperature in hydrolysis experiment. The Zymark TuborVap®LV Evaporator was employed to condense the extracted solution.

Because the thiamethoxam has high water solubility, the standard solution (500mg/l) can be prepared by adding the thiamethoxam into the water directly. 500mg thiamethoxam was weighed precisely and put into measuring flask (1000ml), and then deionized water distilled from potassium permanganate was added into the measuring flask to graduation. Buffer solutions (Yang, 1994) were prepared as follows:
pH=7.0 29.6ml 0.1mol/l NaOH + 50ml 0.1mol/l K_2HPO_4; pH=8.0 46.8ml 0.1mol/l NaOH + 50ml 0.1mol/l K2HPO4; pH=9.0 21.3ml 0.1mol/l NaOH + 50ml 0.1mol/l HBO_3 (0.1mol/l KCl); pH=10.0 43.9ml 0.1mol/l NaOH + 50ml 0.1mol/l HBO_3(0.1mol/l KCl).

2ml standard solution of thiamethoxam was measured by pipet and added into 100ml measuring flask, then buffer solutions of pH= 6, 7, 8, 9 were added into the measuring flask to graduation separately to prepare the solution of 10mg/l. In order to restrain the growth of bacterial, the measuring flasks were sterilized in an autoclave at 121℃ and 0.2g NaN_3 was added into every measuring flask. The solution prepared were place into three water bath which temperature maintained at 25 ± 1℃, 35 ± 1℃, 45 ± 1℃ separately for the duration of experiment. 10ml aliquot of hydrolysis sample was added into 150ml separating funnel, then

the solution was extracted with 10ml redistilled dichloromethane three times. The three extracted solutions were added into the same test tube and were evaporated to dryness in Zymark TuborVap®LV Evaporator, after which 1ml aliquot of deioned water was added into the tube to dissolve the residue which served as the sample for analyzing with HPLC. During evaporating, the temperature maintained at 40℃ and the ultrapure nitrogen gas served as shielding gas. All extractions were performed in triplicate and the results were averaged.

The hydrolytic rate was determined by monitoring the rate of disappearance of thiamethoxam. The sample's analyses were performed on a HP1100 high performance liquid chromatography equipped with diode array detector, Zorbax-C18 column (250mm × 4.6mmID). Injection volume: 20 μ l; Column temperature: 25℃; mobile phase: water/acetonitrile (80/20, 1.0ml/min); detector: 254nm. The thiamethoxam retention time: 5.796min.

The sample hydrolyzed completely was extracted by dichloromethane. The dichloromethane containing the product from the thiamethoxam hydrolysis was analyzed with GC-MS after being dried with sodium sulfate. Helium was used as carrier gas (1.0ml/min). Split injection (ratio = 50:1) of 1 μ l were made at the inlet temperature of 230℃. The oven program was as follows: isothermal at 50℃ for 2min, followed by heating from 50℃ to 180℃ at 10℃/min, finally isothermal at 180℃for 20min.

RESULTS AND DISCUSSION

The sample of pH 7 and pH 8 were measured for 90days, the pH 9 for 9 days and pH10 for 4 days at 25℃. The results are showed in Table 1. From the Table 1 we can see that the thiamethoxam hydrolyzed very slowly at pH 7 and 8. Only 7% of thiamethoxam was hydrolyzed within 90 days at pH=7 and about 40% of thiamethoxam disappeared within 90 days at pH=8. With concentration of OH^- increasing, the hydrolysis of thiamethoxam accelerates. At same temperature of 25℃, the hydrolysis rate of thiamethoxam at pH 8, 9 is far faster than that at pH 7, which show that the hydrolysis of thiamethoxam is a kind of base catalyzed process. Because few available data about the hydrolysis of thiamethoxam at pH=7 were acquired, the equation of thiamethoxam hydrolysis at pH=7 isn't available.

The equations in Table 2 result from data of thiamethoxam hydrolysis at pH=8, 9, 10. From the Table 2, we can see that the hydrolysis of thiamethoxam fit the first-order kinetic equation. The results of thiamethoxam hydrolysis at different temperature are showed in Table 3, from which we can see that the hydrolytic rate of thiamethoxam rise with the temperature rising at pH=8, 9, 10; At the same temperature, the hydrolytic rate of thiamethoxam rise with pH rising. The experimental data were fitted with orgin7.0. The results of the data fitting are shown in Table 4, from which we can see that the hydrolysis of thiamethoxam fit the first-order kinetic. The relationship between temperature and reaction constant

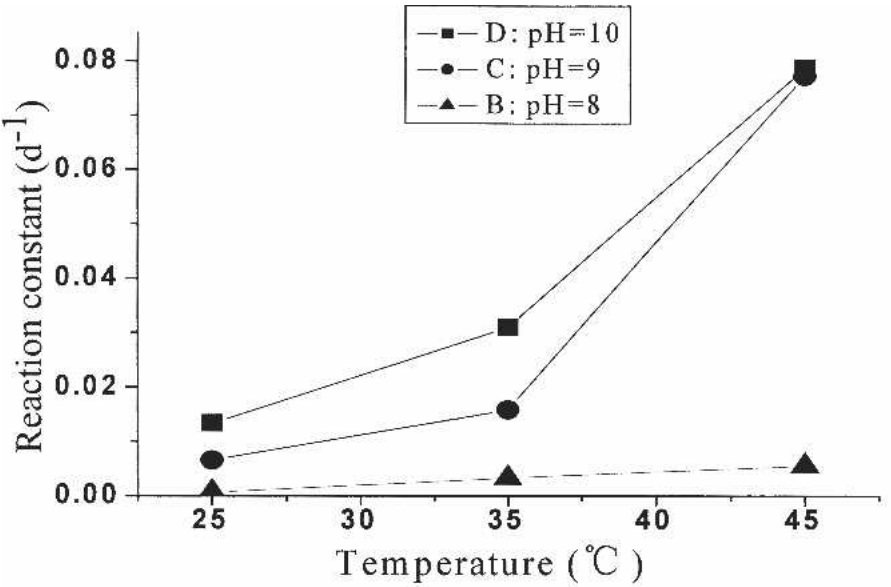

Figure 2. Reaction constant of thiamethoxam hydrolysis at different temperatures.

Table 1. The hydrolysis of thiamethoxam at 25℃.

Time (d)	Concentration of thiamethoxam (mg/L)			
	pH = 7	pH = 8	pH = 9	pH = 10
0	10.000	10.000	10.000	10.000
1	-	-	9.422	6.883
2	-	-	7.822	5.084
3	-	-	6.903	3.728
4	-	-	5.181	2.713
5	-	-	4.914	-
6	-	-	4.250	-
7	-	-	3.480	-
8	-	-	3.080	-
9	-	-	2.477	-
10		9.107		
30	9.806	6.050		
60	9.649	3.640		
90	9.302	2.450		

Table 2. The equations of thiamethoxam hydrolysis at 25℃.

Sample	equation	Reaction rate constant (k)	Half- lives of hydrolysis ($t_{0.5}$)	R
pH=8	lnC =2.3154–0.0162t	0.0164	42.78d	0.9972
pH=9	lnC =2.3443–0.1524t	0.1524	4.55d	0.9957
pH=10	lnC =2.2788–0.3222t	0.3222	2.15d	0.9993

Table 3. Hydrolysis of thiamethoxam at different pHs and temperatures.

Time (h)	Concentration of thiamethoxam (mg/L)								
		pH=8			pH=9			pH=10	
	25℃	35℃	45℃	25℃	35℃	45℃	25℃	35℃	45℃
0		10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000
6		-		-	-	6.619	-	-	6.240
12		-	-	-	-	3.728	-	6.733	3.853
18		-	-	-	-	2.512	-	-	2.423
24		9.235	8.688	9.422	7.192	1.603	6.883	4.513	1.517
48		-	7.901	7.822	5.468		5.084	2.184	
72		8.109	6.673	6.903	4.063		3.728	1.070	
96		7.448	5.755	5.181	2.010		2.713		
120		7.360	4.973	4.914	1.582				
144		6.404	4.358	4.250					
168		5.824	3.808	3.480					
192		5.181	3.281	3.080					
240	9.107								
720	6.050								
1440	3.640								
2160	2.450								

Table 4. Equation of thiamethoxam hydrolysis at different pHs and temperatures.

Sample		Equation	Reaction constant (k)	Half-lives ($t_{0.5}$)	R
pH = 8	25℃	$\ln C = 2.3154 - 6.748 \times 10^{-4} t$	6.748×10^{-4}	1027.19h	0.9972
	35℃	$\ln C = 2.3191 - 0.0033t$	0.0033	210.05h	0.9887
	45℃	$\ln C = 2.2823 - 0.0056t$	0.0056	123.78h	0.9956
pH = 9	25℃	$\ln C = 2.3564 - 0.0066t$	0.0066	105.03h	0.9956
	35℃	$\ln C = 2.3738 - 0.0159t$	0.0159	43.59h	0.9873
	45℃	$\ln C = 2.3048 - 0.0771t$	0.0771	8.99h	0.9984
pH = 10	25℃	$\ln C = 2.2772 - 0.0134t$	0.0134	51.72h	0.9994
	35℃	$\ln C = 2.2777 - 0.0310t$	0.0310	22.36h	0.9998
	45℃	$\ln C = 2.2988 - 0.0785t$	0.0785	8.83h	0.9999

was displayed in Figure 2. From the Figure 2, the conclusions can be made that the reaction constant rise with the temperature rising at certain pH; at 45℃, the

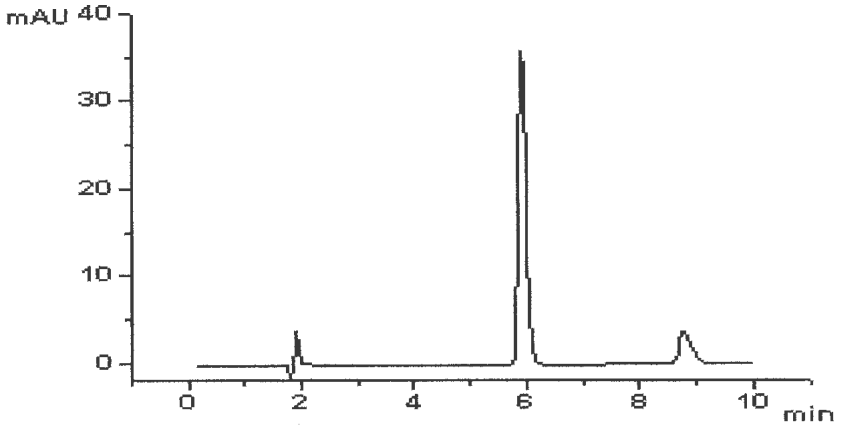

Figure 3. Chromatograms of thiamethoxam hydrolysis (a: thiamethoxam; b: Hydrolytic product of thiamethoxam).

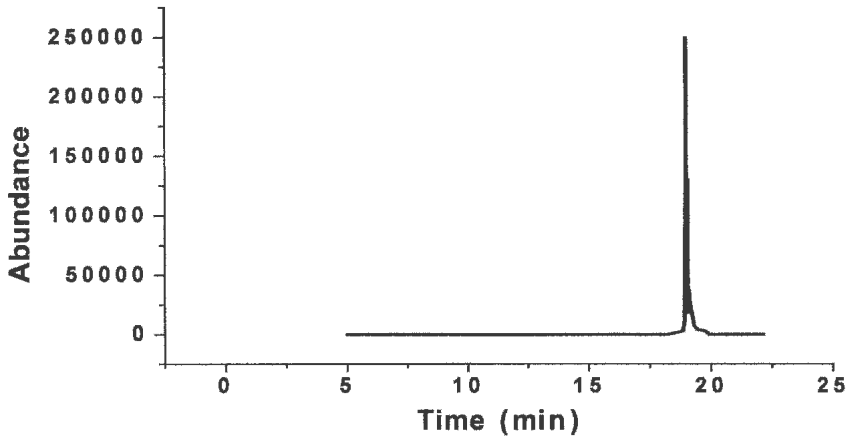

Figure 4. Total ion chromatogram of product of thiamethoxam hydrolysis.

reaction constant of hydrolysis of the solution of pH=9 and pH=10 are approximately equal, which indicates that when the concentration of OH- reach a certain level, the reaction constant of thiamethoxam hydrolysis is determined by temperature.

The HPLC pattern of aqueous thiamethoxam after hydrolysis is shown in Figure 3. From Figure 3, there is only one hydrolytic product apart from the thiamethoxam. The retention time of this hydrolytic product was longer than that of thiamethoxam. No further hydrolytic product peaks were observed during the subsequent degradation of the thiamethoxam, and the hydrolytic product remained stable thereafter. It was concluded that there was only one main hydrolytic product of thiamethoxam in basic media, and it was stable in alkaline solution and not easily decomposed.

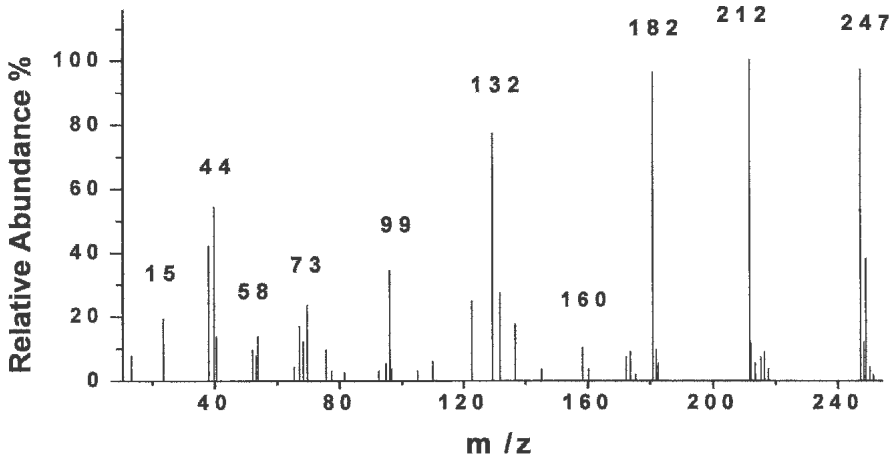

Figure 5. EI mass spectrum of hydrolysis product of thiamethoxam.

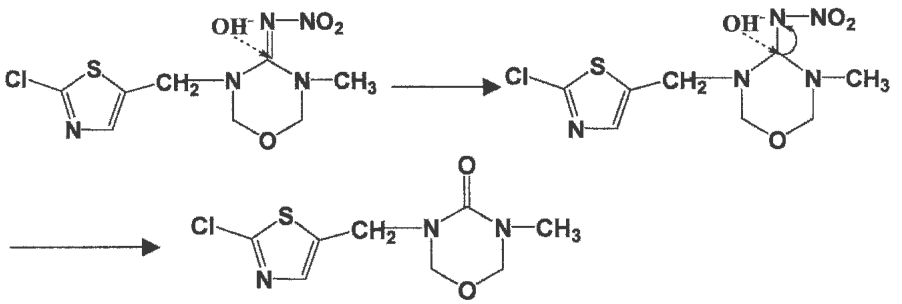

Figure 6. Proposed mechanism for hydrolysis of thiamethoxam.

The completely hydrolyzed solution was assayed via GC-MS in electron impact (EI). The results were shown in Figure 4 and Figure 5. By comparing HPLC retention time and MS spectrum of the isolated hydrolytic product, the hydrolytic product was shown to be 3-(2-chloro-thiazolyl-5-ylmethyl)-5-methyl-4-oxo-oxadiazine.

According to the structure of hydrolytic product, the possible thiamethoxam hydrolytic pathway (Figure 6) was proposed. Owing to the strong electron withdrawing character of the NO_2 group, a small positive change (δ^+) is induced on the carbon of the C-N group of the oxadiazine ring, so that it is readily attacked by OH^-.

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