Hydrolytic dynamics of pesticide N'-(2,4-dimethylphenyl)-N-methylformamidine in aquatic solution

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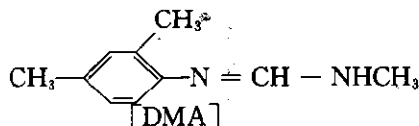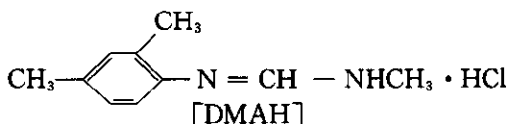
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Abstract—— The hydrolytic dynamics of pesticide N'-(2,4-dimethylphenyl)-N-methylformamidine (DMA) in aquatic solution and its degradation in simulated aquatic ecosystem were investigated. The results showed that the compound was not very stable in aqueous solution and easily decomposed in alkaline solution. It was stable below pH5 and there was obvious tendency that the compound was easily decomposed when pH was greater than 6. The reaction rate constant of DMA increased with increasing of either pH value or temperature of reaction medium. The half-life values of hydrolysis for DMA at 25℃ were 15.92 days at pH 6, and 1.40 days at pH 9, respectively. The temperature coefficient and activation energy of hydrolysis for DMA was 2.9 and 78.74kJ. mol^{-1}, respectively. The degradation of DMA in simulated aquatic ecosystem was similar to that in buffer solution in the laboratory. The half-life values of degradation for DMA at 26℃ in simulated aquatic ecosystem were 3.23 days at pH 9.13 and 1.41 days at pH 8.28, respectively.

Keywords: pesticide; N'-(2,4-dimethylphenyl)-N-methylformamidine; hydrolysis; degradation.

1 Introduction

N'-(2,4-dimethylphenyl)-N-methylformamidine hydrochloride (DMAH) is a newly, high efficacy organonitrogen insecticide and miticide. It is first put into commercial use here in China. The active ingredient of DMAH is N'-(2,4-dimethylphenyl)-N-methylformamidine (DMA). The structure are as follows:

CH₃—〈benzene ring with CH₃〉—N = CH — NHCH₃ · HCl
[DMAH]

CH₃—〈benzene ring with CH₃〉—N = CH — NHCH₃
[DMA]

The pesticide DMHA is mainly used against mite in cotton, soybean, tea, orange, apple fruit and so on.

Some investigators had mentioned compound DMA which was a degradation product of N'-(2,4-methylphenyl)-N-(2,4,dimethylphenyl) formamidine. However, very little literature about the degradation of DMAH or DMA could be available. The hydrolytic dynamics of DMA in aquatic solution and degradation of DMAH in simulated aquatic eco-system were re-

ported in this paper.

2 Materials and methods

2.1 Chemicals

Aqueous solution of 25% DMAH was supplied by Chihui Chemical Factory of Wuhan, Hubei Province. DMA was precipitated by neutralized with sodium hydroxide in aquatic solution of DMAH and purified by recrystalization in cyclohexane for three times. The purity of DMA was greater than 98%.

Methanol and dichloromethane used were analytical grade and were distilled.

2.2 Equipment

pHS-2 model pH meter, LB 801 superous thermostat, LC-3A model high performance liquid chromatography(Shimadzu) with 254 nm UV photometer and stainless steel column 25cm × 4.6mm(i.d.) packed with C_{18}, mobile phase (methanol: water = 80:20, V/V).

2.3 Experiment

The hydrolysis rates of DMA with different of concentrations and solutions of different pH value in buffer solution were studied.

2.3.1 Kinetics

Buffer solutions covering the range between pH 3.0—9.0 were prepared. A sodium hydroxide solutions of the desired hydroxyl ion concentration were also prepared. The half-life value was calculated according to the following equation:

$$T_{1/2} = 0.693/k_1,$$

where k_1 was pseudo-first-order rate constant, the second order rate constant k_2 was calculated from the equation:

$$k_2 = k_1/[OH^-].$$

The pesticide DMA was hydrolyzed in buffer solutions and in sodium hydroxide solutions according to the following procedures, respectively.

2.3.2 Hydrolysis of DMA in buffer solution

2 ml DMA standard solution with concentration of 1.0 mg/ml in methanol was pipetted into 100ml brown-ampules, and was dried to less than 1 ml, different buffer solution was added into ampules, respectively, and kept in the thermostant at 25℃. DMA in solution was analyzed by HPLC at intervals. Each time, duplicated solution 10ml was dropped out, the pH value of solution was adjusted to pH 13 by adding 1 mol/L NaOH solution, extracted with 3×20 ml dichloromethane, the organic phase was dried over anhydrous Na_2SO_4 concentrated to dryness, dissolved in methanol and subjected to HPLC analysis.

Recovery of DMA in water was 95.5±0.6%(2—50 μg/ml), C.V. was 0.6%. The limited detected concentration of DMA in water was 0.01 μg/ml.

2.3.3 Hydrolysis of DMA in different concentration of sodium hydroxide

2 ml DMA standard solution was pipetted into 100ml brown-ampules and dried to less than 1 ml and sodium hydroxide at different concentration was added, respectively, and then kept in the thermostat at 25℃ for 30 min. The DMA in solution was analyzed by HPLC at

intervals.

2.3.4 The determination of active energy of hydrolysis for DMA in solution

2ml DMA standard solution was pipetted into 100ml brown- ampules and was dried to less than 1 ml. A certain concentration of sodium hydroxide was added and hydrolysed at 15, 20, 25, 30, 35 ℃, respectively.

2.3.5 Degradation of DMAH in simulated aquatic ecosystem

Simulated aquatic ecosystem was made of glass-steel with 3 meter in length, 1 meter in width and 1 meter in height. Water grass and algae and so on were bred. Some amount aqueous solution of 25% DMAH was put into the water. Agitator at the bottom of water through was started to stir 1 hour and DMAH could be dispersed thoroughly in water. DMAH in water was analyzed duplicatly by HPLC at intervals.

3   Results and discussion

3.1 Hydrolysis of DMA in buffer solution

The results of hydrolysis of DMA in buffer solutions are in Table 1. The disappearance curve of DMA in buffer solution is presented in Fig. 1. The results showed that DMA is stable at PH3 and 5. However, it is easily decomposed when pH≥6. Hydrolysis rate constant increases with increasement of the pH value of reaction medium. The half-life values of hydrolysis for DMA are 15.92, 6.99, 2.47 and 1.40-day, respectively at pH=6, 7, 8 and 9. It is apparent that DMA is somewhat stable at acidic solution or weak acidic solution and tend to degrade un-

Fig. 1   Hydrolysis of DMA in alkaline solution (25℃)

der neuter solution and easily decomposes under strong alkaline solution. In terms of above statement, DMA is less stability compared to Aldicarb and CCU(Mo, 1986; Yang, 1992).
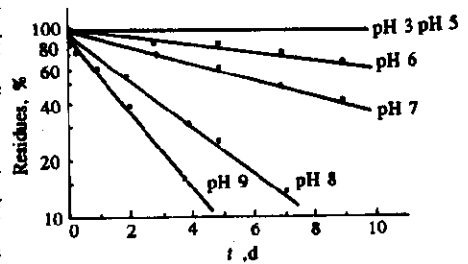
Table 1   Hydrolysis of DMA in buffer solution(25℃)

pH	t, d	K, d^{-1}	$T_{1/2}$, d	r
3	0—56			
5	0—56			
6	0—12	4.35×10^{-2}	15.92	−0.9849
7	0—9.0	9.92×10^{-2}	6.99	−0.9980
8	0—6.0	2.81×10^{-1}	2.47	−0.9716
9	0—4.0	4.85×10^{-1}	1.40	−0.9047

3.2 Hydrolysis of DMA in alkaline conditions

Hydrolysis of DMA in alkaline solution at 25℃ is shown in Table 2 and in Fig. 2. Results showed that hydrolysis rate constant increased with the increasement of concentration

of hydroxyl. This corresponded to the general principle of reaction of organic compound. The relationship between the hydrolysis rate constant of DMA and the concentration of sodium hydroxide is as follows (Fig. 3):

$$K = 46.876 \, C_{OH^-} + 0.283, \quad (n = 5, \ r = 0.9693).$$

here, $C_{OH^-} = 1.334 \times 10^{-3} - 1.334 \times 10^{-2} \, mol/L$.

Table 2   Hydrolysis of DMA in alkaline solution (25°C)

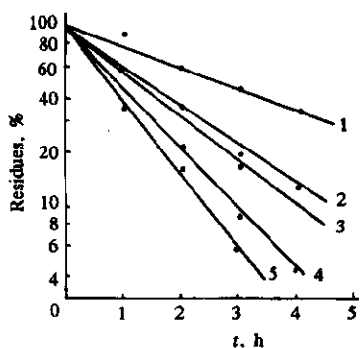| C_{OH^-}, $10^{-3} mol/L$	t, h	K, h^{-1}	$T_{1/2}$, h	r
1.334	0—4	0.276	2.51	−0.987
2.668	0—4	0.494	1.40	−0.997
6.670	0—4	0.598	1.16	−0.981
11.110	0—4	0.756	0.92	−0.982
13.340	0—4	0.936	0.74	−0.990

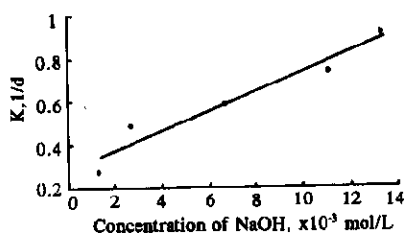Fig. 2   Hydrolysis of DMA in alkaline solution (25°C)

Fig. 3   Effect of temperature of sodium hydroxide on hydrolytic rate of DMA

3.3   Effect of temperature on hydrolysis rate of DMA

Effect of temperature on hydrolysis rate of DMA is obvious and it is shown in Table 3, Fig. 4 and Fig. 5.

Table 3   Effect of temperature on hydrolytic rate of DMA [NaOH]= $1.334 \times 10^{-3} mol/L$

Temp. °C	t, h	K_1, h^{-1}	K, $h^{-1} \cdot L \cdot mol^{-1}$	r	Q	E, kJ/mol
15	0—4	6.47×10^{-2}	48.50	−0.882	2.92	78.74
20	0—4	1.86×10^{-1}	139.40	−0.997		
25	0—4	2.76×10^{-1}	206.82	−0.987		
30	0—4	4.21×10^{-1}	314.84	−0.992		
35	0—4	6.13×10^{-1}	459.70	−0.976		

When temperature increases 10 degree, hydrolysis rate constant increases 1.9 times ($Q = K(t+10)/K(t) = 2.9$). This is close to Aldicarb, Aldicarb Sulfoxide, and CCU ($Q=$

2.5—2.9). The reaction active energy of hydrolysis for DMA calculated from Arrheius equation is 78.74 kJ/mol. The relationship between hydrolysis rate and temperature is described as follows:

$$\ln K = 36.9957 - 9.4753 \times 10^3 1/T \ , \ (\ n = 5, \ r = -0.9747)\ .$$
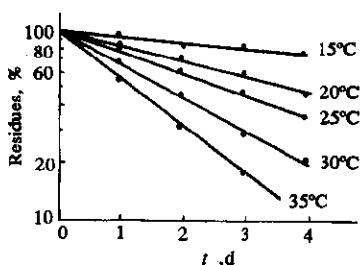

Fig. 4   Hydrolysis of DMA at different temperature
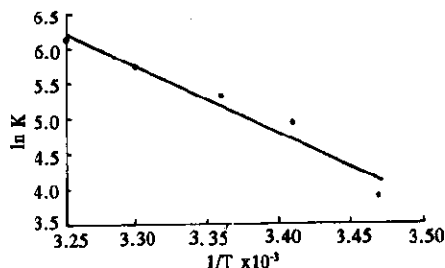[NaOH] = 1.334 × 10⁻³mol/L

Fig. 5   Effect of temperature on hydrolytic rate of DMA
[NaOH] = 1.334 × 10⁻³ mol/L

3.4   Persistence of DMAH in simulated aquatic ecosystem

Studies had been done in two water trough. The initial application amount of pesticide DMAH was the same. pH value of water in two water trough were subtle different. The initial pH value of water trough I and II was 9.13 and 8.26, respectively. The temperature was 26℃. Content of DMAH in water was detected at intervals. The changement of amount of DMAH in water with time is shown in Table 4 and is depicted in Fig. 6. The half-life values are 33.86h and 77.40h for water trough I and I, respectively.
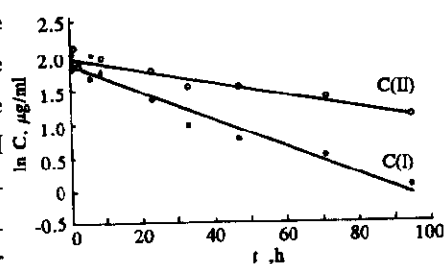

Fig. 6   Degradation of pesticide DMA in simulated water ecosystem

Table 4   Degradation of pesticide DMAH in simulated water ecosystem(26℃)

t, h	Conc. (I),μg/ml		Conc. (I), μg/ml	
	Range	Average	Range	Average
0	7.50—7.52	7.51±0.01	8.06—8.44	8.25±0.19
1	7.19—7.54	7.37±0.17	5.61—6.58	6.10±0.48
3	5.96—6.49	6.22±0.26	5.96	5.96
6	5.18	5.18	6.93—7.54	7.24±0.30
9	5.61—5.79	5.70±0.09	6.58—7.02	6.80±0.22
23	3.73—3.82	3.78±0.04	5.67—5.81	5.74±0.07
33	2.50—2.76	2.63±0.13	4.08—5.04	4.56±0.48
47	2.06—2.19	2.12±0.06	4.47—4.65	4.56±0.09
71	1.45—1.89	1.67±0.22	3.86	3.86
95	1.01—1.05	1.03±0.02	2.54—3.42	2.98±0.44

This was close to the results under laboratory conditions. The degradation rate of DMAH in water trough I was faster than that in trough II due to different pH value in two water trough. The concentration change of DMAH in water through I and II against time could be expressed by following equations, respectively.

$$Pot \ I \ 0-95h: lnC = -2.0471 \times 10^{-2}t + 1.8718$$
$$T_{1/2} = 33.86(h), \ r = -0.9811$$
$$Pot \ I \ 0-95h: lnC = -8.9508 \times 10^{-3}t + 1.9402$$
$$T_{1/2} = 77.44(h), \ r = -0.9463$$

4 Conclusions

Hydrolysis of pesticide was correlated to its persistence in environment. It was an important critical to affect the ultimate fate of pesticide in environment . It was also an important critia to assess the pollution of pesticide in environment.

The results indicated that pesticide DMA was unstable in water. It was relatively stable under acidic or weak acidic conditions. However, it seemed to hydrolyse on neuter conditions and easily decomposed at alkaline conditions .

The results at simulated aquatic ecosystem and laboratory condition were closely. At pH 6 and pH 9, the half-life value of DMAH were 15. 92d and 1. 40 d, respectively. There would be no persistence pollution in the water environmental because of application of pesticide DMAH.

However, some more attention should be paid to the degradation products of DMA .

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