ピレスロイド系殺虫剤サイパーメスリンの水中における加水分解

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Original Article

Hydrolysis of the Pyrethroid Insecticide Cypermethrin in Aqueous Media

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Hydrolysis of (1*R*, *cis*, *αRS*)- and (1*R*, *trans*, *αRS*)-isomers of cypermethrin [(*RS*)-*α*-cyano-3-phenoxybenzyl (1*RS*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] was studied in buffer solutions at pH 3.0, 7.0 and 11.0, and in natural river and sea water at 15°C, 25°C, 40°C and 55°C under laboratory conditions. For making suitable approximations, the expressions for k_A, k_N and k_B of Eq. (1) were calculated, using values of k_H at three pH's. $k_H = k_A[H^+] + k_N + k_B[OH^-]$ (1). The pH-rate profile thus obtained showed that hydrolysis of both isomers proceeded predominantly through neutral (pH independent) and base-catalyzed processes in the regions below pH 5.0 and above pH 7.0, respectively, whereas both reactions occurred between pH 5.0 and 7.0. The *trans*-isomer was hydrolyzed approximately 1.2–1.7 times faster than the *cis*-isomer at any pH tested between 25°C and 50°C. The rates of hydrolysis of both isomers in buffer solutions were similar to those in one sample of river and one sample of sea water. The cleavage of the ester linkage proceeded more rapidly than the hydration of the CN group at any pH and temperature tested.

INTRODUCTION

Cypermethrin [NRDC 149, (*RS*)-*α*-cyano-3-phenoxybenzyl (1*RS*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], (**I**), a mixture of eight isomers owing to three chiral centers (cyclopropyl C-1 and C-3, and the benzylic carbon atom), has proved to be effective for the control of insect pests in cotton, top fruits and vegetable crops.[1] **I** is two to three times more active than permethrin,[1-3] and (1*RS*)-*cis*-isomer is more insecticidally active than (1*RS*)-*trans*-isomer by a factor of two.[4] From the viewpoint of environmental safety, studies on metabolism of **I** in plants,[5-7] soils,[8-11] rats[12-14] and mice[15,16] as well as photodegradation[17] in water and on soil surface have already been performed.

For a better understanding of the fate in aqueous media, hydrolysis of (1*R*, *cis*, *αRS*)- and (1*R*, *trans*, *αRS*)-**I** was examined in various buffer solutions at pH 3.0, 7.0 and 11.0 and in natural river and sea water.

MATERIALS AND METHODS

1. *Chemicals*

The (1*R*, *cis*)- and (1*R*, *trans*)-**I** labeled with ^{14}C separately at the cyclopropyl C-1 (referred to as cyclopropyl-^{14}C), cyano (^{14}CN) or benzyl ring (uniform labeling, benzyl-^{14}C) were synthesized at the Takarazuka Research Center, Sumitomo Chemical Co., Ltd.[18] The specific activities were as follows: cyclopropyl-^{14}C-**I**; 22.0 mCi/mmol, benzyl-^{14}C-**I**; 25.2 mCi/mmol. Each preparation had more than 99% radiochemical purity as determined by thin-layer chromatography (TLC), followed by autoradiography and liquid scintillation counting (LSC). The following unlabeled chemicals were used for reference standards: (*RS*)-*α*-Carbamoyl-3-phenoxybenzyl (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (**II**), (*RS*)-*α*-carboxy-3-phenoxybenzyl (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-

Table 1 TLC *Rf* values of cypermethrin (**I**) and its degradation products.

Chemical	*Rf* value			
	A	B	C	D
(1*RS*, *cis*, *αRS*)-**I**	0.43, 0.48	0.84	0.67	0.68
(1*RS*, *trans*, *αRS*)-**I**	0.36, 0.40	0.84	0.67	0.68
cis-**II**	0.0	0.28, 0.31	0.25, 0.28	0.14, 0.16
trans-**II**	0.0	0.27, 0.29	0.23, 0.26	0.13, 0.15
cis-**III**	0.0	0.34, 0.37	0.57	0.17, 0.20
trans-**III**	0.0	0.33, 0.34	0.54	0.17, 0.19
cis-**IV**	0.02	0.26	0.57	0.45
trans-**IV**	0.01	0.26	0.57	0.38
V	0.43	0.45	0.69	0.61
VI	0.0	0.29	0.52	0.32

A: hexane/diethyl ether (20/1), B: hexane/toluene/acetic acid (3/15/2), C: benzene saturated with formic acid/diethyl ether (10/3), D: toluene/diethyl ether/acetic acid (75/25/1).

Table 2 Composition of buffer solutions used in the experiment.

pH (22°C)	5.0 M NaCl (ml)	1.0 M Glycine +1.0 M NaCl (ml)	2.0 N HCl (ml)	0.5 M Na_2HPO_4 (ml)	4.0 M NaH_2PO_4 (ml)	2.0 M NaOH (ml)	Total (*l*)	Ionic strength (*μ*)
3.0	3.2	3.2	0.4				1	0.02
7.0	3.2			2.3	0.2		1	0.02
11.0	3.2	2.0				1.0	1	0.02

dimethylcyclopropanecarboxylate (**III**), (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropanecarboxylic acid (**IV**), 3-phenoxybenzaldehyde (**V**) and 3-phenoxybenzoic acid (**VI**).

2. Thin-layer Chromatography (TLC)

Precoated silica gel 60 F_{254} chromatoplate (20×20 cm, a layer 0.25 mm thick, E. Merck) were used for analytical and preparative purposes. The solvent systems used, and the *Rf* values of **I** and its degradation products are listed in Table 1. The degradation products were located by autoradiography and the unlabeled reference compounds were visualized by UV fluorescence quenching.

3. Radioassay

Liquid scintillation counting (LSC) and autoradiography were carried out according to the procedures reported previously.[19]

4. Procedure for Hydrolysis of Cypermethrin

Buffer solutions with almost the same ionic strength (*μ* 0.02) were prepared by dissolving the component salt in distilled water at the rate shown in Table 2. The pH of the solutions was adjusted to the desired values at 15°C, 25°C, 40°C and 50°C, and checked with a pH meter model F-7AD (Horiba Co., Ltd.) calibrated with standard buffer solutions. Natural water was collected at the Muko River (pH 8.27 at 25°C) and the seaside in Nishinomiya (pH 8.17 at 25°C), Hyogo Prefecture, and sterilized through a 0.1 *μ*m filter paper (No. 85 SB, 60 mm in diameter, Toyo Roshi Co., Ltd.) immediately before use. (1*R*, *cis*)- and/or (1*R*, *trans*)-[^{14}C]-**I** in acetonitrile (1 ml) was added to buffer solution or natural water (99 ml) in a 100 ml Erlenmeyer flask with a ground glass stopper, which had been preheated to the desired temperature and shaken for 3 min by a mechanical shaker to attain a level of 5 ppb (water solubility, 8.9 ppb at 25°C). Each

flask was immersed in a thermostatic water bath, protected from light, at 15°C, 25°C, 40°C and 55°C. At specified intervals, the whole volume of the reaction mixture (100 ml) was extracted three times with a twofold volume of ethyl acetate after acidified to pH 2 with 1 N HCl. The combined extract was washed with a saturated aqueous sodium chloride solution, radioassayed, dried over anhydrous sodium sulfate and evaporated to less than 0.2 ml, the whole volume of which was subjected to silica gel TLC. The reaction mixture was sampled four times in duplicate with one observation made after one-half of the chemicals was hydrolyzed or 4 weeks, whichever was shorter.

RESULTS AND DISCUSSION

The pseudo-first-order rate constants (k_H) and half-lives ($T_{1/2}$) of hydrolysis of (1*R*, *cis*)- and (1*R*, *trans*)-**I** in buffer solutions and natural water were determined by a linear regression analysis using Eq. (1),

$$k_H = t^{-1} \ln (C_t/C_0) \qquad (1)$$

where C_0 and C_t were the concentrations of the isomers remaining in buffer solutions at zero time and time t, respectively. The value of C_0 was assumed to be 99.8, which was the radiochemical purity (%) of both isomers, and the values of C_t were expressed as percent of the applied ^{14}C. In dilute aqueous solutions in the present study, the rate of hydrolysis obeys the pseudo-first-order kinetics and is dependent upon only the substrate concentration. Therefore, the hydrolysis rate constant can be expressed as follows:

$$k_H = k_A[H^+] + k_N + k_B[OH^-] \qquad (2)$$

where k_A and k_B are the second-order rate constants and k_N is a first-order rate constant. At a given pH, Eq. (2) contains three unknown, k_A, k_B and k_N. Therefore, these quantities were determined by measuring the values of k_H at three different pH's at a fixed temperature. The rate constants k_A, k_B and k_N were calculated by using the three measurements at pH 3.0, 7.0, and 11.0 as follows (Table 3):

$$k_A = 10^3 k_H(3.0) - 10^3 k_H(7.0) + 10^{-1} k_H(11.0) \qquad (3)$$

$$k_N = k_H(7.0) - 10^{-4} k_H(3.0) - 10^{-4} k_H(11.0) \qquad (4)$$

$$k_B = 10^{-15-pK_W} k_H(3.0) - 10^{-11-pK_W} k_H(7.0) + 10^{-11-pK_W} k_H(11.0) \qquad (5)$$

where $k_H(x)$ (x=3.0, 7.0 or 11.0) is the hydrolysis rate constant at a pH value of x and K_W is the ionization constant of water.

The temperature dependence of k_A, k_N and k_B was determined using the Arrhenius Eq. (6),

$$k = A \exp(-E/RT) \qquad (6)$$

where A is the preexponential factor and E the activation energy. The Arrhenius parame-

Table 3 Rate constants of acid-catalyzed (k_A), neutral (k_N) and base-catalyzed (k_B) hydrolysis of (1*R*, *cis*, *RS*)- and (1*R*, *trans*, *RS*)-cypermethrin (**I**).

Chemical	Temp. (°C)	Rate constant					
		k_H (sec^{-1})			k_A ($sec^{-1}\ M^{-1}$)	k_N (sec^{-1})	k_B ($sec^{-1}\ M^{-1}$)
		pH 3	pH 7	pH 11			
cis-Isomer	15	—	—	1.21×10^{-4}	—	—	—
	25	6.16×10^{-9}	3.63×10^{-8}	3.02×10^{-4}	6.00×10^{-8}	6.10×10^{-9}	3.02×10^{-1}
	40	1.21×10^{-8}	1.21×10^{-7}	1.09×10^{-3}	1.00×10^{-7}	1.20×10^{-8}	3.74×10^{-1}
	50	1.72×10^{-8}	2.49×10^{-7}	2.32×10^{-3} [a]	2.00×10^{-7}	1.70×10^{-8}	4.24×10^{-1}
trans-Isomer	15	—	—	2.22×10^{-4}	—	—	—
	25	8.69×10^{-9}	5.91×10^{-8}	5.05×10^{-4}	9.00×10^{-8}	8.60×10^{-9}	5.05×10^{-1}
	40	1.62×10^{-8}	1.78×10^{-7}	1.62×10^{-3}	2.00×10^{-7}	1.60×10^{-8}	5.55×10^{-1}
	50	2.13×10^{-8}	3.40×10^{-7}	3.19×10^{-3} [a]	3.00×10^{-7}	2.10×10^{-8}	5.83×10^{-1}

[a] The value was calculated using the Arrhenius expression at pH 11.

Table 4 Temperature dependence of rate constants of acid and base-catalyzed (k_A and k_B) and neutral (k_N) hydrolyses of (1*R*, *cis*, α*RS*)- and (1*R*, *trans*, α*RS*)-cypermethrin (**I**).

Chemical	Arrhenius expression	Activation energy (kcal/mol)	r_2[a)]
cis-Isomer	$\log k_A = -0.694 - 1.95\times10^3\ T^{-1}$	8.94	0.951
	$\log k_N = -2.42\ -1.73\times10^3\ T^{-1}$	7.90	0.998
	$\log k_B = 1.39\ -5.69\times10^2\ T^{-1}$	2.60	1.00
trans-Isomer	$\log k_A = -0.235 - 2.03\times10^3\ T^{-1}$	9.28	0.998
	$\log k_N = -2.99\ -1.51\times10^3\ T^{-1}$	6.92	0.993
	$\log k_B = 5.15\ -2.42\times10^2\ T^{-1}$	1.11	0.998

a) Coefficient of determination.

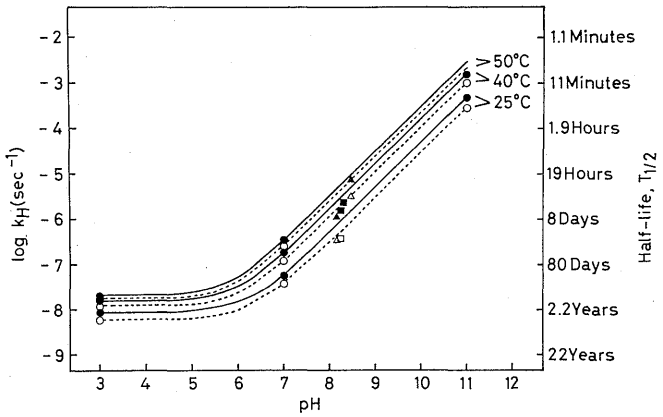


Fig. 1 pH profile of hydrolysis of (1*R*, *cis*, α*RS*)- and (1*R*, *trans*, α*RS*)-cypermethrin (**I**). ···, —: calculated (the *cis*- and *trans*-isomers, respectively), ○, ●: observed (the *cis*- and *trans*-isomers, respectively), □, ■: river water (the *cis*- and *trans*-isomers, respectively), △, ▲: sea water (the *cis*- and *trans*-isomers, respectively).

ter are shown in Table 4.

Figure 1 shows the pH dependence of hydrolysis of both isomers by a plot of log k_H vs. pH, where log k_H was calculated from Eq. (2) using the Arrhenius parameters shown in Table 4. The half-lives of both isomers by hydrolysis were calculated using Eq. (7).

$$T_{1/2} = k_H^{-1} \ln 2 \qquad (7)$$

Both isomers were unstable under basic conditions, especially at pH 11 and above 15°C with the half-life of less than 2 days. In contrast, they were fairly stable under acidic conditions and the half-life ranged from 378 days (the *trans*-isomer: 50°C) to 1300 days (the *cis*-isomer: 25°C). The *trans*-isomer was hydrolyzed approximately 1.2–1.7 times faster than the *cis*-isomer at any pH tested at 25–50°C. This appears to be due to the less steric hindrance of the *trans*-isomer to the attack by hydroxyl ion, compared with the *cis*-isomer. The hydrolysis of both isomers proceeded through a neutral reaction between pH 3.0 and 5.0, since the k_H was almost independent on pH at any temperature tested. On the other hand, a slope was close to +1 above pH 7.0, and therefore a base-catalyzed process was predominant in this region. Both neutral and base-catalyzed reactions occurred in the range from pH 5.0 to 7.0. These results indicate that the acid-catalyzed hydrolysis is not so important for hydrolysis of both isomers. The calculated log k_H was found to be also applicable to natural river and sea water within ±5% experimental errors (Table 5). It has been reported that humic and fulvic acids in natural water enhanced the acid-catalyzed hydrolysis of atrazine,[20,21] and that

Table 5 Pseudo-first-order rate constants (k_H) and half-life values ($T_{1/2}$) of hydrolysis of (1*R*, *cis*, α*RS*)- and (1*R*, *trans*, α*RS*)-cypermethrin (**I**) in river and sea water.

Medium	Temp. (°C)	pH	*cis*-Isomer		*trans*-Isomer	
			k_H (sec^{-1})	$T_{1/2}$ (days)	k_H (sec^{-1})	$T_{1/2}$ (days)
River water	25	8.27	3.79×10^{-7}	21.2	1.58×10^{-6}	5.08
	40	8.30	2.28×10^{-6}	3.52	2.39×10^{-6}	3.35
Sea water	25	8.17	3.34×10^{-7}	24.0	1.11×10^{-6}	7.22
	40	8.47	3.91×10^{-6}	2.05	7.59×10^{-6}	1.06

a number of alkaline earth and heavy metal ions catalyzed the hydrolysis of a variety of organic esters.[22,23] However, the catalyzed hydrolyses were not observed in the present study.

Thus, the rate constants of hydrolysis of both isomers in water, including natural water, could be expressed by Eq. (2) by using k_A, k_N and k_B listed in Table 4.

A similar pH-rate profile was observed in the hydrolysis of fenpropathrin,[24] fenitrothion,[25] parathion-methyl,[26] DDT,[27] methoxychlor,[27] procymidone[28] and alkyl halides[29,30] such as methyl iodide, methyl bromide and chloroform. Between pH 5.0 and 9.0, the *trans*- and *cis*-isomers of cypermethrin were hydrolyzed approximately 2.5–4.0 and 1.8–2.7 times faster than fenpropathrin, respectively, whose chemical structure is similar to cypermethrin's except the acid moiety.[24]

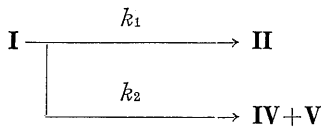
It appears that the carbonyl group of cypermethrin is more susceptible to the nucleophilic attack by a hydroxyl ion than that of fenpropathrin, due to a more significant electron-withdrawing effect of the 2,2-dichlorovinyl group in the acid moiety, compared with that of the dimethyl group of fenpropathrin.

Three major products were formed in buffer solutions and natural water. They were identified as the α-carbamoyl derivative (**II**), 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (**IV**) and 3-phenoxybenzaldehyde (**V**) by TLC cochromatography with the authentic standards. No *cis*/*trans* isomerization of the cyclopropane ring occurred before and/or after the ester linkage cleaved. The other products such as **III** and **VI** were of minor importance in any aqueous solutions tested. Since the rate of the formation of **IV** from the cyclopropyl-^{14}C preparation was nearly the same as that of **V** from the benzyl-^{14}C preparation, the overall hydrolytic reaction scheme for **I** could be expressed as follows:

Table 6 Pseudo-first-order rate constants of hydrolysis of (1*R*, *cis*, α*RS*)- and (1*R*, *trans*, α*RS*)-cypermethrin (**I**) and for formation of **II** (k_1) and **V** (k_2) at 25°C as a function of pH.

Chemical	pH	Rate constant (sec^{-1})		
		k_H	k_1	k_2
cis-Isomer	3.0	6.16×10^{-9}	$0.08\ (0.05)^{a)}\times10^{-9}$	$2.04\ (0.78)\times10^{-9}$
	7.0	3.63×10^{-8}	$0.28\ (0.05)\times10^{-8}$	$2.86\ (0.16)\times10^{-8}$
	11.0	3.02×10^{-4}	$0.13\ (0.01)\times10^{-4}$	$2.81\ (0.04)\times10^{-4}$
	River water	3.79×10^{-7}	$0.25\ (0.15)\times10^{-7}$	$3.15\ (0.47)\times10^{-7}$
	Sea water	3.34×10^{-7}	$0.28\ (0.09)\times10^{-7}$	$2.84\ (0.11)\times10^{-7}$
trans-Isomer	3.0	8.69×10^{-9}	$1.24\ (0.40)\times10^{-9}$	$4.23\ (0.71)\times10^{-9}$
	7.0	5.91×10^{-8}	$0.32\ (0.06)\times10^{-8}$	$5.23\ (0.11)\times10^{-8}$
	11.0	5.05×10^{-4}	$0.16\ (0.01)\times10^{-4}$	$4.73\ (0.05)\times10^{-4}$
	River water	1.58×10^{-6}	$0.13\ (0.11)\times10^{-6}$	$1.33\ (0.17)\times10^{-6}$
	Sea water	1.11×10^{-6}	$0.06\ (0.02)\times10^{-6}$	$0.99\ (0.07)\times10^{-6}$

a) Values in parentheses indicate standard deviations.



where k_1 and k_2 are the pseudo-first-order rate constants for the formations of **II** and **V** (or **IV**), respectively. The rate constants k_1 and k_2 in buffer solutions and natural water at 25°C are listed in Table 6. At any pH and temperature tested, the formation of **V** was significantly rapid in comparison with that of **II**. It appears that the ester bond is more susceptible to both neutral and base-catalyzed hydrolyses than the CN group.

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要　　約

ピレスロイド系殺虫剤サイパーメスリンの水中における加水分解

高橋尚裕，三上信可，松田　正，宮本純之

(1*R*, *cis*, α*RS*)- および (1*R*, *trans*, α*RS*)-サイパーメスリンの緩衝液もしくは自然水中における加水分解について検討した．*trans* 異性体は25～50°C において *cis* 異性体に比べて 1.2～1.7 倍速く加水分解した．両異性体とも，pH 5 以下では水による neutral reaction，pH 7 以上では塩基触媒，pH 5～7 の範囲では両者の反応を受けて分解した．また Arrhenius の式を用いて加水分解速度を温度の関数として表わし，計算から求めた両異性体の加水分解半減期は，自然水中における実測値とよく一致した．加水分解による主反応は両異性体ともエステル結合の開裂であった．