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STUDY OF ALKALINE HYDROLYSIS OF THE INSECTICIDE ALPHAMETHRINE BY ISOTACHOPHORETIC DETERMINATION OF DECOMPOSITION PRODUCTS

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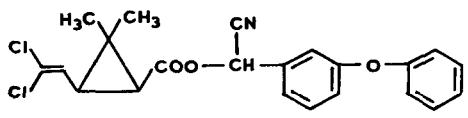
SUMMARY

Alkaline hydrolysis of the pyrethroid insecticide alphamethrine has been studied. After hydrolytic cleavage at various temperatures and pH values, the degradation products, phenoxybenzoic acid and the dichloro derivative of chrysanthemic acid, were identified and determined by means of capillary isotachophoresis . Rate constants, activation energies and the reaction enthalpy and entropy were calculated.

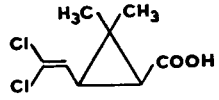
INTRODUCTION

Alphamethrine (I) belongs to the group of pyrethroid insecticides which have recently been widely applied. It is essentially an isomeric form of a substance called cypermethrine.

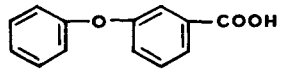
Studies of the determination of pyrethroid insecticides and their residues have



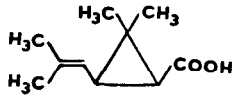
I Alphamethrine



III Dichlorochrysanthemic acid



II m-Phenoxybenzoic acid



IV Chrysanthemic acid

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concentrated especially on separation methods. A number of gas chromatographic methods especially with electron-capture detection[1–8] and several liquid chromatography procedures, especially high-performance liquid chromatography (HPLC)[3,5,7,9–11], have been published for the determination of the content of cypermethrine and its isomers in various materials.

Insecticides from the pyrethroid group undergo a variety of decomposition reactions, *eg.*, photodegradation, hydrolysis and metabolic transformations[11–16]. In the case of alphamethrine, alkaline hydrolysis results in the degradation products II and III which, due to their chemical structure, permit employment of analytical capillary isotachophoresis for the determination.

Capillary isotachophoresis has so far been little used for the analysis of pesticide formulations. However, recently several studies employing this technique have appeared[17,18].

In the present work we have focused on the investigation of the hydrolytic degradation of alphamethrine using isotachophoresis.

EXPERIMENTAL

Pure compounds I–IV were prepared for the isotachophoretic determination of hydrolysis degradation products.

The compound alphamethrine, (*R,S*)-cyano(3-phenoxyphenyl)methyl (*R,S*)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, was isolated from a formulation Vaztak 10 EC (Shell) and repurified by a multiple crystallization from hexane and acetone.

m-Phenoxybenzoic acid was prepared at the Palacký University Olomouc, while compounds III and IV were synthesized at the Institute of Organic Chemistry of the Polish Academy of Sciences (Warsaw, Poland). The purity of the compounds prepared was monitored by elemental analysis.

Calibration solutions of the compounds II–IV at the concentrations $1 \cdot 10^{-5}$–$1.5 \cdot 10^{-3}$ mol l^{-1} were prepared by dissolution in deionized water under mild alkalization.

Solutions of Kolthoff–Vleeschhouwer buffer were used to maintain pH values during hydrolysis: Na_2CO_3 and $Na_2B_4O_7$ (ionic strength $I = 0.15$) for pH 10; Na_2HPO_4 and NaOH ($I = 0.158$ *M* and 0.193 for pH 11 and 12, respectively).

Analytical isotachophoresis

Isotachophoretic determinations were performed on an instrument for capillary isotachophoresis in a two-capillary array ZKI 01 (ÚRVJT Spišská Nová Ves, Czechoslovakia). The driving current in the pre-separation capillary (150 mm × 0.8 mm I.D.) was 250 μA while a current of 30 μA was used in the analytical capillary (150 mm × 0.3 mm I.D.). Separated zones were detected by a conductivity detector the signal of which was recorded on a two-line recorder. The sampling was performed by a microsyringe (Hamilton), volume 5 μl.

The operational systems used are given in Table I.

Alkaline hydrolysis

Alkaline hydrolysis of alphamethrine was carried out in sealed ampoules (10 ml) in an atmosphere of argon. Always, 2.5 ml of buffering solution were added to 2.5 ml of

TABLE I

OPERATIONAL SYSTEMS USED

MES = Morpholinoethanesulphonic acid; PVA = poly(vinyl alcohol).

System	*Leading ion, c (mol l^{-1})*	*Counter ion*	*pH*	*Additive*	*Terminating electrolyte, concentration (M)*
A	Cl^- 10^{-2}	ε-Aminocaproic acid	4.30	0.05% PVA	MES $5 \cdot 10^{-3}$
B	Cl^- 10^{-2}	Creatine	4.80	0.05% PVA	MES $5 \cdot 10^{-3}$
C	Cl^- 10^{-2}	Histidine	6.00	0.05% PVA	MES $5 \cdot 10^{-3}$

alphamethrine solution ($2 \cdot 10^{-2}$ mol l^{-1} in ethanol). After removal of air by a flow of argon, the ampoules were sealed and thermostatted at 30, 35, 40, 45 and 50°C. At intervals of 10 min to 28 h and after cooling, the contents were made up to 50 ml with deionized water in a volumetric flask. A 5 μl volume of this sample was injected into the isotachophoretic analyzer. The concentrations of the degradation products formed upon hydrolysis were found from calibration graphs.

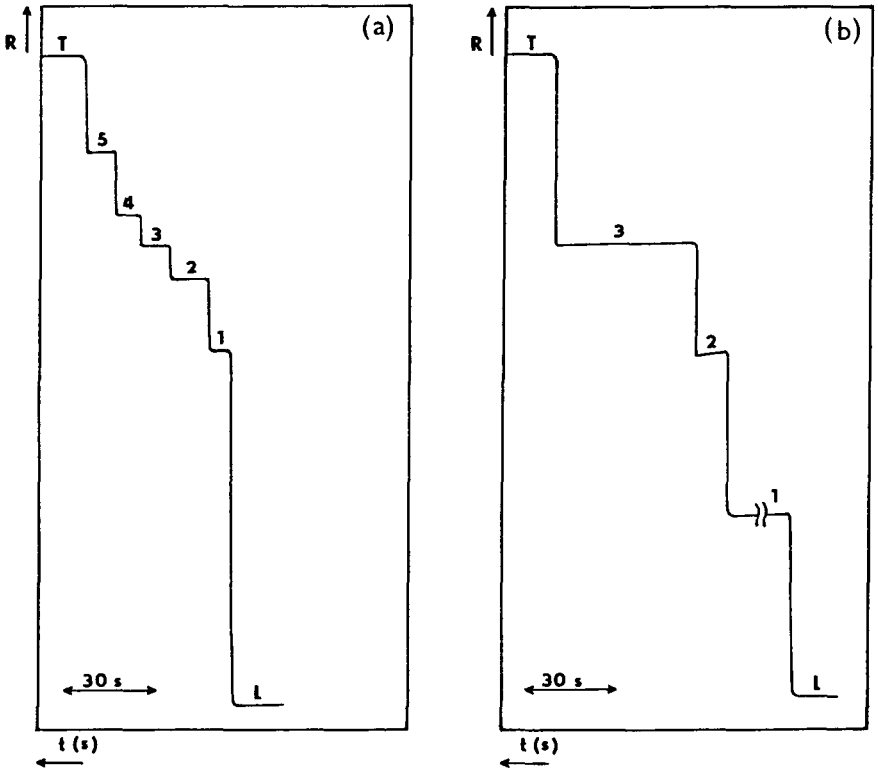

Fig. 1. Separation of degradation products: (a) system B, injection of 5 μl of mixture; 1 = II, 2 = III-*trans*, 3 = III-*cis*, 4 = IV-*trans*, 5 = IV-*cis*; (b) system B, injection of 5 μl of hydrolysate; 1 = PO_4^{3-}, 2 = II, 3 = III-*cis*. L = Cl^-; T = MES; *t* = time; *R* = resistance.

TABLE II
RELATIVE STEP HEIGHTS

Compound	*Heights relative to trichloroacetic acid*		
	System A	*System B*	*System C*
II	1.66	1.69	1.44
III-*cis*	2.08	2.00	1.50
III-*trans*	1.90	1.84	1.50
IV-*cis*	2.36	2.33	1.58
IV-*trans*	2.12	2.05	1.52

RESULTS AND DISCUSSION

Three electrolyte systems (Table I) were tested to choose a suitable separation system for the isotachophoretic determination of compounds II–IV. In systems A–C the separation of all three compounds takes place. In systems A and B, even *cis* and *trans* isomers of compounds III and IV (Fig. 1) are fairly well separated. Separation in systems leading electrolytes of lower pH values ($pH_L = 3.60$) could not be performed due to the low mobilities of the compounds. For single electrolytes the relative zone heights were calculated, relative to trichloroacetic acid (step height 1.00, Table II).

From the isotachophoretically determined concentrations of compounds II and III in hydrolysates, the time dependences were constructed and the recovery upon hydrolysis after 28 h was calculated (Table III). The relative standard deviations of recovery ranged from 1.3 to 2.6% for *cis*-dichlorochrysanthemic acid (III-*cis*) and from 1.7 to 4.0% for *m*-phenoxybenzoic acid (II), respectively (mean of four parallel determinations).

The course of hydrolysis satisfies a first-order kinetic equation from which the values of the rate constants (Table IV) were obtained and their dependence on the reciprocal of the temperature was plotted (Fig. 2). The Arrhenius equation

$$\Delta H = E_A + RT \tag{1}$$

TABLE III
RECOVERY UPON HYDROLYSIS FOR 28 H

Temperature (°C)	*Mean recovery (%)*					
	pH 10		*pH 11*		*pH 12*	
	II	*III-cis*	*II*	*III-cis*	*II*	*III-cis*
30	2.9	13.2	4.5	18.1	7.8	39.2
35	4.3	19.0	4.8	25.3	10.1	45.0
40	5.7	27.3	6.6	32.0	12.8	52.1
45	7.7	35.0	8.8	40.0	18.1	68.4
50	10.0	45.2	12.0	49.3	19.3	93.0

TABLE IV

RATE CONSTANTS, k (AT TEMPERATURE $T = 50°C$), ARRHENIUS EQUATION, ACTIVATION ENTHALPY AND ENTROPY

The k values are given as the means of four parallel determinations; CI = Confidence interval expressed as twice the estimated standard deviation.

pH	$k \pm CI$ *(l/mol · s)*	*Arrhenius equation*	ΔS *(J/mol · K)*	ΔH *(kJ/mol)*
10	$(7.60 \pm 0.12) \cdot 10^{-5}$	$\ln k = 6.00 - 5.00 \cdot 10^3\ T^{-1}$	−202.6	43.8
11	$(1.14 \pm 0.02) \cdot 10^{-4}$	$\ln k = 6.60 - 5.10 \cdot 10^3\ T^{-1}$	−197.6	44.7
12	$(2.35 \pm 0.02) \cdot 10^{-4}$	$\ln k = 7.79 - 5.34 \cdot 10^3\ T^{-1}$	−187.7	46.7

was used for calculation of the activation energy, E_A, and activation enthalpy, ΔH, as well as for activation entropy, ΔS

$$\Delta S = R\,(\ln A - \ln \frac{k_B T}{h} - 1) \tag{2}$$

where A, k_B and h are the frequency factor, Boltzmann and Planck constants, respectively. Calculated values are given in Table IV.

Recovery of *m*-phenoxybenzoic acid from hydrolysates ranged from 2.9 to 19.3% (Fig. 1b), was poorly reproducible and could not be employed for the investigation of the degradation process.

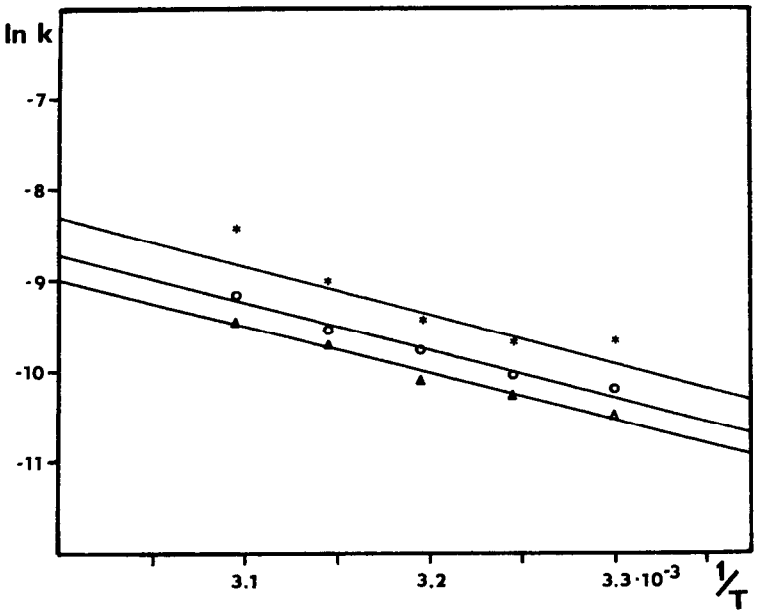

Fig. 2. Graphical expression of the Arrhenius equation. pH 10 (⅓), 11 (@) and 12 (✱).

ACKNOWLEDGEMENTS

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