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Kinetic Study of the Degradation of Ethiofencarb in Aqueous Solutions

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Abstract: A kinetic study of the hydrolysis of ethiofencarb (α-ethylthio-*o*-tolyl methylcarbamate) in pure water and in aqueous solutions at pH 2, 6, 9 and 12 and at three different temperatures (4, 20 and 50(±1)°C) has been carried out using a gas chromatographic nitrogen-phosphorus detection method. The values of the first-order rate constants (k) for the degradation reaction were calculated. The values for k were found to be dependent on pH and temperature. No acid hydrolysis was observed in any case. Complete degradation of ethiofencarb was observed at pH 12 at all three temperatures; it was practically instantaneous at room temperature. Ethiofencarb was also completely degraded at pH 9 at 20 and 50°C, while in pure water (pH 6) degradation took place at 50°C but not at 20°C. Ethiofencarb was not degraded in pure water at lower temperatures and, due to the reversible nature of the reaction, at equilibrium about 80% of the pesticide remained undegraded at room temperature.

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1 INTRODUCTION

The degradation of synthetic organic pesticides begins as soon as they are synthesised and purified. During shipping and storage of these products, breakdown of the principal components may occur due to harsh environmental conditions, prolonged periods of storage or chemical interactions between the parent molecules and the water used in the final mixture.

The processes responsible for the degradation of pesticides can be classified as physical, chemical and biological. Water, a principal reactive agent of chemical degradation, is responsible for considerable breakdown of pesticides in solution, especially in conjunction with pH extremes. For many pesticide molecules, hydrolysis is a primary route of degradation.[1] Heat, thermal decomposition and cold, particularly freezing temperatures, occasionally contribute to pesticide degradation.[2,3]

Systematic studies of the kinetics of pesticide decomposition in aqueous solutions have been reported in the literature.[4,5] These studies provide useful information about the dependence of degradation pathways on several degrading agents, the behaviour of a contaminant in aqueous media and the stability of pesticides in different conditions when used for the preparation and storage of reference certified material used to evaluate the performance of analytical systems.[3] Knowledge of a pesticide's stability in water is important, especially to agricultural and analytical chemists.

Carbamate pesticides constitute an important group of pesticides noted for their relatively short persistence in the environment. This group of pesticides, which act as acetylcholinesterase reversible inhibitors, are an alternative to the organochlorine and organophosphorus products. Carbamate insecticides have therefore become widely used against insects in soil and foliar applications. The *N*-methyl carbamates are thermally labile, which complicates direct gas chromatographic

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determination because of the formation of phenols and other decay products in non-reproducible amounts through thermal degradation occurring inside the injector or the column during the GC run.[6] A liquid chromatographic method has been developed for the analysis of this kind of pesticide, which involves post-column derivatisation and fluorescence detection. However, this analytical method is time-consuming and requires a separate analytical system and the preparation of post-column reagents. The GC thermal degradation of *N*-methylcarbamates may be overcome by using special conditions. Thus, Suzuki *et al.*[7] demonstrated that, when a short wide-bore column was used, the GC degradation of carbamate could be avoided due to the short column residence time. Wigfield *et al.*[8] investigated the chromatographic degradation of seven carbamates using two different columns and two temperature profiles and successfully analysed seven carbamates by using a short DB-5 capillary column with a programmed-temperature vaporizer (PTV) injection technique.

Ethiofencarb (α-ethylthio-*o*-tolyl methylcarbamate) is a systemic insecticide widely used in agriculture because of its specific effect against aphids. A large number of papers have been published about the potential toxicity of ethiofencarb; the maximum permissible dose for humans is 0·01 mg kg^{-1} day^{-1} and the maximum permissible concentration in working areas is 0·05 mg m^{-1}. Since no systematic studies on the kinetics of ethiofencarb degradation in aqueous solution had been reported in the literature, the objective of this paper was to study the kinetics of the hydrolysis of ethiofencarb at several pH and temperature values, employing a gas chromatographic method. Prior to this, a study of the stability of the pesticide under different injection and oven temperatures was carried out.

2 EXPERIMENTAL

2.1 Apparatus

A Hewlett–Packard HP 5890 gas chromatograph equipped with a nitrogen-phosphorus detector (NPD) and an HP Ultra 2 fused silica capillary column (crosslinked 5% phenyl methyl silicone gum phase of 0·33 μm film thickness, 0·2 mm internal diameter and 25 m length) was used for determining the pesticide. For the stability studies, several chromatographic conditions were used. The operating conditions were optimised to separate the components of a commercial ethiofencarb formulation ('Croneton,' Bayer) and these conditions, which also separated ethiofencarb, malathion and diazinon were used for degradation studies. These conditions were: injector temperature 250°C and detector temperature 275°C; the oven temperature programme had an initial temperature of 120°C for 3 min with the temperature programmed to rise at a rate of 60°C min^{-1} to a final temperature of 225°C and be held for 7 min, followed by a second rise at the rate of 60°C min^{-1} to a temperature of 275°C and then held for 5 min. The nitrogen carrier-gas flow-rate was 0·6 ml min^{-1} and the flow-rates for the nitrogen-phosphorus detector were 70 ml min^{-1} (air) and 4 ml min^{-1} (hydrogen); the auxiliary gas flow-rate (nitrogen) was 30 ml min^{-1}. Injection was by split mode with a split vent flow of 30 ml min^{-1} and the sample volume injected was 2 μl.

A thermostatic bath (Selecta), a thermocontroller unit and a refrigerator unit (Selecta) were used to maintain a constant temperature bath. An orbital stirrer equipped with two holders for four flasks each was used for sampling.

2.2 Chemicals

All pesticide standards, certified and 99·9% pure, were obtained from Riedel-de-Häen (Seelze, Germany). All the solvents used were HPLC or PRS grade quality; methyl isobutyl ketone (MIBK) from Fluka, chloroform, acetone, xylene and ethyl acetate from Carlo Erba. Hydrochloric acid, sodium hydroxide, sodium carbonate and sodium hydrogen carbonate were from Merck and anhydrous calcium chloride from Carlo Erba.

2.3 Solutions

Pesticide solutions: stock solutions of 1·00 mg ml^{-1} of diazinon; 10·2 mg ml^{-1} of ethiofencarb and 20·7 mg ml^{-1} of malathion were prepared in acetone. The more dilute solutions were prepared by dilution with the solvent as required.

Different pH solutions were prepared with double-distilled, sterilised water. The final pH was then adjusted to the desired values as follows: NaOH 0·01 M for pH 12, and the buffer solutions $NaHCO_3/Na_2CO_3$ for pH 9 and HCl/KCl for pH 2. The pH value for the 510 μg ml^{-1} ethiofencarb solution was 6.

The aqueous solutions were prepared by diluting 2·50 ml of 10·2 mg ml^{-1} solution of ethiofencarb into 50 ml with different pH media, so that the acetone content of the final solution was 50 ml $litre^{-1}$ and the ethiofencarb concentration was 510 μg ml^{-1}. This concentration was chosen because it is that recommended for the application of the commercial formulation of ethiofencarb.

2.4 GC stability studies

The gas chromatographic stability of ethiofencarb was studied by injecting individual solutions of ethiofencarb

(3·00 μg ml^{-1}) and diazinon as internal standard (2·00 μg ml^{-1}) into the gas chromatograph with different profiles of injection and isothermal column oven temperatures. The lowest injection and oven temperatures tested were 225 and 175°C respectively, while the highest temperatures were 275 and 225°C. Statistical study of the peak area measurements obtained from the different temperature profiles supported the conclusion that no significant degradation occurred.

The operating conditions were selected to obtain the separation of the components of a solution of a commercial ethiofencarb formulation and are described above. The injection temperature selected was set at 250°C (to ensure a complete evaporation). Under these conditions, ethiofencarb did not show any degradation.

2.5 Quantification

Quantitative determinations of ethiofencarb and malathion solutions in MIBK were carried out by the internal standard (diazinon 2·00 μg ml^{-1}) method. The detection limits were: 1·00 μg ml^{-1} for ethiofencarb and 0·50 μg ml^{-1} for malathion. Both areas and heights were used for the quantification. The RSD values for ethiofencarb (10 determinations) were 2·8% and 3·2% for area and height respectively, with corresponding figures of 2·9% and 2·4% for malathion.

2.6 Extraction study

The liquid-liquid extraction method was chosen, as it is a simple and reliable method for quantification of pesticides in water. In order to select the best solvent for extracting ethiofencarb from the aqueous phase, a study of extractions with different solvents and different stirring times was made. Several solvents of different polarities (MIBK, ethyl acetate, chloroform and xylene) were tested and measurements of the pesticide extracted after 15 and 30 min were made. Studies were carried out in quadruplicate for each solvent and each stirring time tested. Malathion was used as the internal standard for the extraction procedure. Extraction recoveries were obtained from the following equation:

$$\% \text{ pesticide extracted} = \frac{C_e}{C_{th}} \times 100$$

where C_e is the pesticide concentration in the final solution and C_{th} the theoretical final concentration.

A solution of ethiofencarb, 510 μg ml^{-1}, was prepared in double-distilled and sterilised water. Aliquots of 1 ml each were acidified with hydrochloric acid (1 M) to pH 2 and 310·5 μg of malathion were added (15 μl of malathion stock solution). Aliquots were extracted with the different solvents. After 15 or 30 min stirring, the phases were separated and the organic phases were dried with anhydrous calcium chloride. The drying agent was then removed and the internal standard (diazinon) was added to an aliquot of 25 μl. The final volume was adjusted to 1 ml (the concentration of diazinon in this solution being 2 μg ml^{-1}). Two microlitres of the solutions were injected into the chromatograph and the concentrations of ethiofencarb and malathion were measured. The standard solutions used for the calibration were made up in the same solvents as used for the extracts. C_{th} values for ethiofencarb and malathion were 12·75 and 7·76 μg ml^{-1}, respectively.

The results are shown in Table 1. The ethiofencarb extraction recoveries were dependent on stirring time and were lower with increased time, except when MIBK was used. The analysis of variance statistical treatment (ANOVA) showed that there were no significant differences between the use of 15 or 30 min stirring when ethiofencarb was extracted with MIBK. Malathion extraction recoveries were high in all cases and no differences were found relating to time dependence. When the extraction was carried out in 15 min, the ethiofencarb and malathion recoveries showed a difference depending on the solvent used; ethiofencarb extraction recoveries differed significantly between 15 and 30 min stirring time for solvents other than MIBK. The extraction solvent chosen was, therefore, MIBK with a stirring time of 15 min.

TABLE 1
Average Extraction Recoveries Obtained for Ethiofencarb and Malathion at pH 6 and 20(±1)°C

Pesticide	*Extraction time (min)*	*Recovery (%) (±SD)*			
		Ethyl acetate	*Chloroform*	*MIBK*	*Xylene*
Ethiofencarb	15	141·0 (±5·9)	98·5 (±9·7)	92·5 (±1·5)	101·5 (±4·5)
	30	86·0 (±4·6)	81·0 (±4·1)	91·0 (±1·1)	88·0 (±1·2)
Malathion	15	88·2 (±11·1)	120·7 (±4·1)	89·5 (±1·0)	123·0 (±3·2)
	30	92·7 (±1·1)	131·2 (±1·1)	89·2 (±0·2)	118·0 (±1·4)

Analysis of variance (ANOVA) was applied to the extraction time effect. For ethiofencarb, all the solvents showed significant recovery differences when extracted over 15 as opposed to 30 min, except MIBK. (P = 95%).

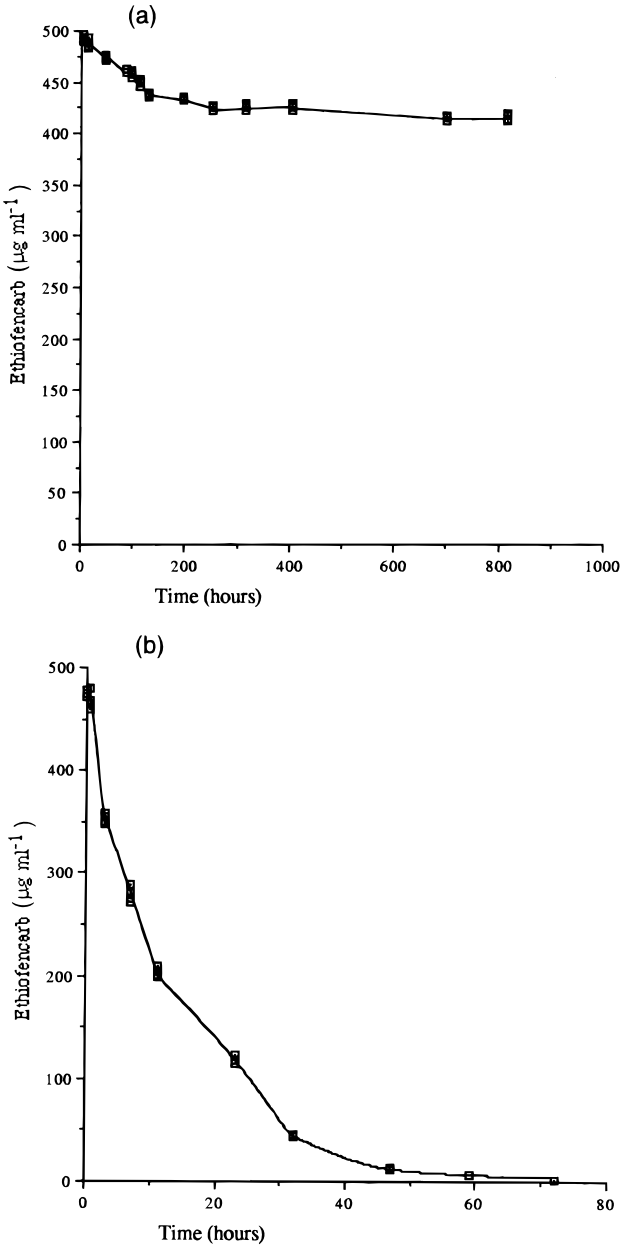

Fig. 1. Ethiofencarb decay observed at pH 6; (a) at room temperature (20(±1)°C) and (b) at 50(±1)°C.

Extraction recoveries were tested for the rest of the pH values and temperatures, using MIBK as the solvent and 15 min stirring. The procedure was the same as described above. Average ethiofencarb recoveries were over 95% (the highest RSD was 2·5%) for all the pH and temperature values except for pH 12, at which recoveries ranged from 76(±1·3)% at 4(±1)°C to 36(±1·2)% at 50(±1)°C. These low recoveries can be explained by taking into account the fast reaction rates in strong alkaline media and the time involved in taking the sample. Malathion average recoveries were higher than those obtained at pH 6, probably due to the higher salinity of the buffer solutions, and they ranged from 101% to 109%, with a highest RSD of 1·6%.

2.7 Decay studies

Ethiofencarb aqueous solutions, prepared as described above, were kept in constant temperature baths of 4, 20 and 50(±1)°C and in the total absence of light. Each pH solution was prepared in duplicate, and the duplicates sampled together. Samples were taken at different times.

The sample treatment procedure was as follows: 1 ml of the reactive solution was acidified to pH 2 to stop the reaction, then the internal standard (malathion) was added in quantities ranging from 10·8 μg to 310·5 μg, depending on the amount of subsequent dilution required for the sample. The extraction procedure was then applied. An aliquot of the organic extract between 25 μl and 100 μl (volume increased with degraded pesticide) was taken and diazinon was added to obtain a final concentration of 2·00 μg ml^{-1} in all cases. The final volume was adjusted to obtain a dilution ranging from 1/40 (highest concentrations of ethiofencarb) to 1/1·25 (lowest concentrations of ethiofencarb). The solutions obtained were injected into the chromatograph.

2.8 Determination of kinetics parameters

To determine the kinetics of the degradation, plots of concentration against time were made and an exponential regression analysis was then performed on each data set in which the pesticide was completely degraded. The rate constant, k, was calculated from the first-order rate equation:

$$C_t = C_0 e^{-kt}$$

where C_t represents the concentration of pesticide at time t, C_0 represents the initial concentration (both concentrations expressed in μg ml^{-1}) and k is the rate constant in hours^{-1}. The half-life ($t_{1/2}$) was determined from the equation for each experiment. The confirmation of the first-order rate kinetics was derived from the linearity of the plots of ln C_t against time (graphic method).

The decrease in ethiofencarb concentration with time was also used to calculate the kinetic rate constant (k) according to the equation:

$$dt = -k \frac{dC}{C}$$

For a time interval between t_1 and t_2, the integrated equation yields as follows:

$$k = \frac{\ln \dfrac{C_1}{C_2}}{\Delta t} \quad (1)$$

where Δt is the time interval $(t_1 - t_2)$ and C_1 and C_2 are the pesticide concentrations (μg ml^{-1}) at times t_1 and t_2, respectively.

3 RESULTS AND DISCUSSION

3.1 Decay study

Data were collected for all the pH values at the three temperatures selected, to a total time of 34 days, exceeding the safety interval (21 days) given for ethiofencarb by 13 days. For each data collection, two samples were taken and processed as described above. Figures 1 to 3 show the degradation of ethiofencarb at the different pH and temperature values.

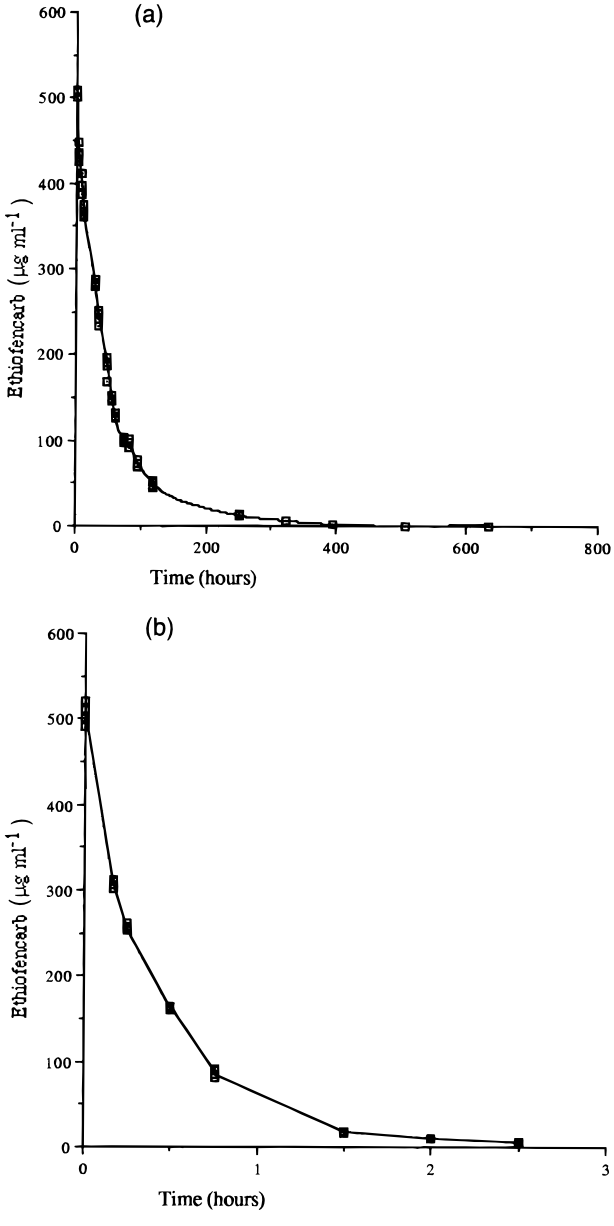

Fig. 2. Ethiofencarb decay observed at pH 9; (a) at room temperature and (b) at 50(±1)°C.

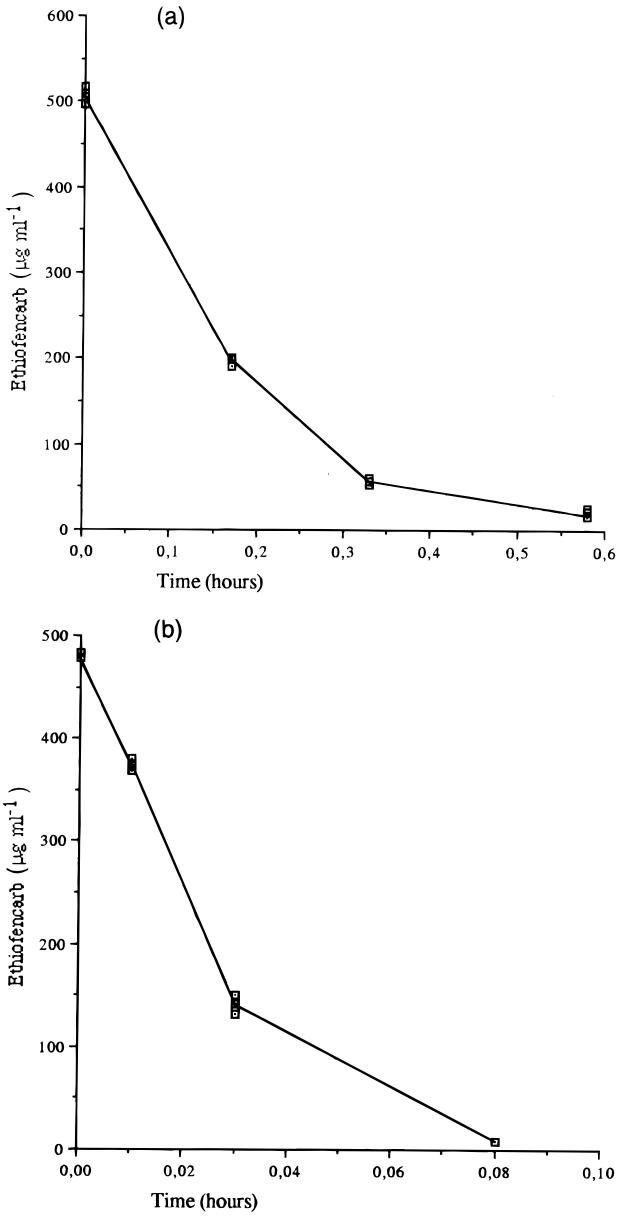

Fig. 3. Complete decay of ethiofencarb at pH 12 at the following temperatures: (a) 4(±1)°C, (b) 20(±1)°C (Degradation at 50(±1)°C was almost identical to Fig. 3(b)).

At *room temperature* (20(±1)°C), 80% of the initial ethiofencarb was present in the solution at the end of the study at pH 6, with decay being observed during the first eight days of reaction and the concentration remaining constant afterwards. Complete degradation of ethiofencarb was observed at pH 9 and 12; this was reached in less than 10 min at pH 12, while at pH 9 it was reached after 25 days. The pesticide was not degraded at pH 2. At *high temperature* (50(±1)°C), the degradation of ethiofencarb occurred at pH 6, 9 and 12. At pH 6, the pesticide was not detected after four days from the beginning of the reaction, while alkaline degradation was faster and did not exceed 2 h at pH 9 or 5 min at pH 12. At this temperature, acid degradation was not observed either. Only strongly basic media (pH

TABLE 2
Values of k and $t_{1/2}$ Obtained for Ethiofencarb Hydrolysis

	k (s^{-1})			$t_{1/2}$ (s)		
T(°C) / pH	4	20	50	4	20	50
6	—	—	$2{\cdot}2 \times 10^{-5}$ [a] $2{\cdot}1 \times 10^{-5}$ [b]	—	—	$3{\cdot}2 \times 10^{4}$ [a] $3{\cdot}3 \times 10^{4}$ [b]
9	—	$5{\cdot}8 \times 10^{-6}$ [a] $6{\cdot}1 \times 10^{-6}$ [b]	$6{\cdot}1 \times 10^{-4}$ [a] $6{\cdot}4 \times 10^{-4}$ [b]	—	$1{\cdot}2 \times 10^{6}$ [a] $1{\cdot}1 \times 10^{6}$ [b]	$1{\cdot}2 \times 10^{3}$ [a] $1{\cdot}1 \times 10^{3}$ [b]
12	$1{\cdot}6 \times 10^{-3}$ [a] $1{\cdot}6 \times 10^{-3}$ [b]	$>1{\cdot}3 \times 10^{-2}$	$>1{\cdot}3 \times 10^{-2}$	432[a] 432[b]	<0·72	<0·72

At pH 2, the pesticide was not degraded at any of the temperatures studied.
At pH 12 and temperatures of 20 and 50(±1)°C, the degradation was instantaneous.
[a] Values calculated by the graphic method.
[b] Values calculated by using eqn (1).

12) produced the degradation of ethiofencarb at *low temperatures* (4(±1)°C). At this pH, the pesticide concentration was lower than 0·01% of the initial ethiofencarb in less than 1 h from the beginning of the reaction.

As expected, the degradation was accelerated in basic media and at high temperatures.

3.2 Kinetics

Using the graphical method described above, k values and half-life times for the different conditions were obtained. The k values were also calculated by using eqn (1). The equations calculated for the degradation of ethiofencarb and half-lives are shown in Table 2.

Table 3 shows the results of typical kinetic experiment for the degradation of ethiofencarb by using eqn (1). The k values so calculated at different time intervals compared well in those cases in which the pesticide was completely degraded, except at pH 12 and 20 and 50(±1)°C, where the reaction occurs instantaneously.

TABLE 3
Results of a Typical Kinetic Experiment of the Degradation of Ethiofencarb, at pH 6 and 50(±1)°C

Time (min)	C_{Et}($\mu g\ ml^{-1}$)	k (s^{-1})
0	479	
		$2{\cdot}2 \times 10^{-5}$
180	377	
		$1{\cdot}9 \times 10^{-5}$
420	285	
		$1{\cdot}9 \times 10^{-5}$
660	217	
		$2{\cdot}1 \times 10^{-5}$
1920	43	
		$2{\cdot}2 \times 10^{-5}$
2820	13	
		$2{\cdot}0 \times 10^{-5}$
3540	5·5	
		$2{\cdot}3 \times 10^{-5}$
4320	1·9	

Mean k value $2{\cdot}1 \times 10^{-5}\ s^{-1}$, with RSD of 7·1%.

A theoretical model for the alkaline hydrolysis of *N*-methylcarbamate pesticides was proposed by Katagi.[9] The observed first-order kinetics for the reaction agree with the mechanisms proposed by Katagi, taking into account the fact that the pH was constant through time; the pH value measured at the end of the hydrolysis did not show variation from the initial value. The degradation rate increased with the increase of the initial OH^- ion concentration; at room temperature and in strong alkaline media, the reaction occurred instantaneously.

The rate is also affected by the temperature (T); the dependence of k on temperature is given by the equation:

$$k = \Delta e^{-\beta/T}$$

where Δ and β are constants that depend on the reaction's nature. As shown, increased temperature gave an exponential rise of the reaction rate.

It was observed that in neutral conditions of pH and temperature (pH 6 and 20(±1)°C), complete hydrolysis did not occur. The pesticide showed an initial decay followed by a stabilisation of the ethiofencarb concentration in the solution, because of the reversible nature of the reaction. Table 4 shows data on the decomposition of ethiofencarb at pH 6 and 20(±1)°C. As shown, the rate constant (reported as k_1) calculated by using eqn (1) did not show approximate constancy similar to that obtained in other conditions. Equilibrium was reached in approximately eight days, with about 80% of the ethiofencarb remaining intact. In the same way as reported by Sing *et al.*[4] for the reversible decomposition of benomyl, it was possible to calculate the rate constant (k_2) for the forward degradation reaction after the

TABLE 4
Application of Eqn (1) to the Degradation of Ethiofencarb at pH 6 and 20(±1°C)

Time (min)	$C_{Et}(\mu g\ ml^{-1})$	$k_1\ (s^{-1})$	$C_{Et} - C_{Et}\ (eqn)$	$k_2\ (s^{-1})$
0	495		50	
		$3{\cdot}9 \times 10^{-7}$		$6{\cdot}7 \times 10^{-8}$
260	492		47	
		$3{\cdot}6 \times 10^{-7}$		$6{\cdot}4 \times 10^{-8}$
740	487		42	
		$2{\cdot}5 \times 10^{-7}$		$6{\cdot}4 \times 10^{-8}$
2800	471		26	
		$1{\cdot}9 \times 10^{-7}$		$7{\cdot}5 \times 10^{-8}$
5080	459		14	
		$1{\cdot}7 \times 10^{-7}$		$7{\cdot}5 \times 10^{-8}$
6700	454		9	
		$1{\cdot}1 \times 10^{-7}$		
11640	445			
15010	445			

Rate constant for the forward degradation reaction (k_2) based on ethiofencarb concentration at time t minus ethiofencarb concentration at equilibrium (Mean k_2 value $6{\cdot}9 \times 10^{-8}\ s^{-1}$, with RSD of 8·1%).

concentration at infinite time (equilibrium) was subtracted from the concentration at time t (Table 4).

The equilibrium was not reached at high temperatures for the same pH value where the degradation of ethiofencarb was complete. The total degradation of ethiofencarb was reached in all the basic media, except at pH 9 and low temperature. This shows that low temperatures can stabilise ethiofencarb solutions provided the pH is not too high.

4 CONCLUSIONS

The results obtained clearly indicate that ethiofencarb degradation occurs in an exponential way over time at high temperatures and alkaline media, in which the kinetics can be fitted to a first-order rate equation. The degradation reaction is reversible at 20(±1)°C and pH 6.

The reaction rate is strongly affected by pH and temperature. Degradation at 20(±1)°C is about 100 times slower than at 50(±1)°C and a 100-fold increase in the hydrolysis rate occurs from pH 6 to 9 (maintaining constant temperature).

Standard solutions of ethiofencarb in aqueous media can be prepared or stabilised by acidifying solutions. Ethiofencarb dissolved in acid media should remain intact for a longer time if stored at low temperatures. Even at high temperatures acidic ethiofencarb solutions will be stable for a month.

Strong alkaline solutions of the pesticide are very unstable and cannot be stabilised with low temperatures. Ethiofencarb degradation in these media occurs instantaneously even at room temperature, making the correct calculation of a k value impossible with the instrumentation available in our laboratory.

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REFERENCES

1. Lartiges, S. B. & Garrigues, P. P., Degradation kinetics of organophosphorus and organonitrogen pesticides in different waters under various environmental conditions. *Environ. Sci. & Technol.*, **29** (1995) 1246–54.
2. Vink, J. P. M. & Vanderzee, S. E. A. T. M., Some physicochemical and environmental factors affecting transformation rates and sorption of the herbicide metamitron in soil. *Pestic. Sci.*, **46** (1996) 113–19.
3. Barcelo, D., House, W. A., Maier, E. A. & Griepink, B., Preparation, homogeneity and stability studies of freeze-dried water-containing pesticides. *Intern. J. Environ. Anal. Chem.*, **57** (1994) 237–54.
4. Singh, R. P., Brindle, I. D., Hall, C. D. & Chiba, M., Kinetic study of the decomposition of methyl [1-(butylcarbamoyl)-1*H*-benzimidazol-2-yl] carbamate (benomyl) to methyl 1*H*-benzimidazol-2-ylcarbamate (MBC). *J. Agr. Food Chem.*, **38** (1990) 1758–62.

5. Cavalier, T. C., Lavy, T. L. & Mattice, J. D., Persistence of selected pesticides in ground-water samples. *Ground Water*, **29** (1991) 225–31.
6. Färber, H. & Schöler, H. F., Gas-chromatographic determination of carbamate pesticides after flash-heater methylation with trimethylsulfonium hydroxide. *J. Agr. Food Chem.*, **41** (1993) 217–20.
7. Suzuki, O., Hattori, H., Liu, J., Seno, H. & Kumazawa, T., Positive-ion and negative-ion mass-spectrometry and rapid cleanup of some carbamate pesticides. *Forensic Sci. Int.*, **46** (1990) 169–80.
8. Wigfield, Y. Y., Grant, R. & Snider, N., Gas chromatographic and mass spectrometric investigation of seven carbamate insecticides and one metabolite. *J. Chromatogr. A*, **657** (1993) 219–22.
9. Katagi, T., In *Rational approaches to structure, activity and ecotoxicology of agrochemicals*, **33** (1993) 310–19.