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Degradation of Carbaryl in Natural Waters: Enhanced Hydrolysis Rate in Micellar Solution

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The massive use of pesticides for agricultural, domestic and industrial purposes and their potential hazard to the consumers' health justify the need for more information about their behavior towards physical, chemical and biological factors in order to understand their degradation, persistence and metabolism in the environment.

Carbaryl, N-methylcarbamate 1-naphthyl ester, is a useful broad spectrum insecticide whose persistence in the environment may vary between one and several weeks. In water, carbaryl degrades to 1-naphthol. Among the factors that have an influence on the hydrolysis rate are pH, temperature and the presence of microorganisms (Mount and Oehme 1981; Wolfe et al. 1978).

Many organic substances, including molecules of biological interest, form organized systems in solution. These organized systems may greatly modify the rate of some bimolecular reactions. Hexadecyltrimethylammonium bromide (HDTAB) is a surfactant capable of forming micellar solutions whose interactions with carbaryl and 1-naphthol have been previously studied (Ayala et al. 1991). In the present paper the influence of some experimental conditions on the rate of hydrolysis of carbaryl is studied in an HDTAB micellar medium in natural waters. As both carbaryl and 1-naphthol fluoresce under UV-irradiation, fluorimetric measurements were chosen to monitor the hydrolysis reaction of carbaryl.

MATERIALS AND METHODS

All chemicals used were of analytical reagent grade. The carbaryl reference solution was prepared from a USEPA standard product (99.7%), in absolute ethanol.

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Table 1. The characteristics of the natural water samples analyzed.

Samples	pH	S.C.(µS/cm)*	Hardness(mg/L $CaCO_3$)
1	7.78	2410	380
2	8.21	7000	190
3	8.35	863	135
4	8.70	923	282
5	8.90	1669	115

* Specific Conductivity.

Water samples were collected from wells (2) and public water supply coming from wells (1, 3, 4, and 5) in the South of Tenerife, in 1-L amber glass bottles with Teflon liners and stored no more than a week at 4°C. Table 1 shows the characteristics of the water samples studied.

The hydrolysis rate of carbaryl in aqueous and micellar media was monitored by measuring the variation in fluorescence intensity versus time of carbaryl solutions in 10% or 40% (v-v) ethanol-water media, containing the surfactant concentration chosen at the suitable hydroxyl ion concentration adjusted with sodium hydroxide solution, and thermostated at 25±0.1°C, at maximum excitation and emission wavelengths (Ayala et al. 1991).

For monitoring the hydrolysis rate of carbaryl in natural waters, 0.5 mL of carbaryl reference solution, 1.5 mL of 0.1 M HDTAB or 1.5 mL distilled water were added into a 50 mL measuring flask, and made up to mark with the natural water under study previously filtered (0.45 µm). Fluorescence intensity variations at 25±0.1°C were recorded in the experimental conditions indicated above.

All fluorescence measurements were made with a Perkin Elmer MPF-44A recording spectrofluorimeter calibrated daily by use of the Perkin-Elmer set of fluorescent polymer blocks.

RESULTS AND DISCUSSION

To study the hydrolysis of carbaryl it is necessary to use aqueous-organic media due to the low solubility of carbaryl in water. The use of carbaryl solutions in 10% and 40% (v-v) ethanol-water media allows to study the influence of the organic solvent on the degradation of the insecticide. These media guarantee that the solubilization of carbaryl is not due to the influence of the micellar systems. In all cases solutions containing hydroxyl ion excess with regard to carbaryl are used. The hydroxyl ion concentrations are determined from the corrected pH values (Bates et al. 1963) according to the ethanol percentages of solutions.

Table 2. Kinetic parameters for the alkaline hydrolysis of carbaryl in ethanol-water media, at 25±0.1°C.

$\lvert OH^-\rvert \cdot 10^4$ (M)	$k_1(min^{-1})\cdot 10^2$	$t_{0.5}$(min)
10%(v-v)EtOH-H_2O		
1.6	10.06	6.0
0.6	3.92	17.7
0.3	1.98	35.0
40%(v-v)EtOH-H_2O		
6.2	7.34	9.3
4.1	3.58	17.8
1.9	1.87	36.9
1.2	1.17	56.2

The pseudo-first order constants (k_1) and the time to reach 50% hydrolysis ($t_{0.5}$) shown in Table 2 have been calculated using the following equation: $\ln (F_t-F_\infty) = \ln (F_0-F_\infty) - k_1 t$, where F are the intensities of the fluorescence emitted by carbaryl and 1-naphthol from solutions of carbaryl in 10% and 40% (v-v) ethanol-water media, at 25±0.1°C, and at several hydroxyl ion concentrations obtained by adding suitable amounts of sodium hydroxide solutions.

On plotting log k_1 versus log $\lvert OH^-\rvert$ straight lines are obtained, whose slopes near 1 indicate that the hydrolysis reaction of carbaryl follows a first order kinetics with regard to the hydroxyl ion concentration. From the $k_2 = k_1/\lvert OH^-\rvert$, the second order constants $(6.5\pm0.4)\cdot 10^2$ and $(1.0\pm0.2)\cdot 10^2$ $L\cdot mol^{-1}\cdot min^{-1}$ are calculated for the 10% and 40% (v-v) ethanol-water media, respectively. These results point out the remarkable inhibitory effect played by ethanol on the hydrolysis rate of carbaryl.

Comparing the values of k_1 and $t_{0.5}$ obtained for each series of solutions, 10% or 40% (v-v) ethanol-water, it is observed the great influence of the hydroxyl ion concentration on the reaction. It is also established that for $\lvert OH^-\rvert > 10^{-3}$ the hydrolysis is too fast to be measured by fluorimetric methods, while for $\lvert OH^-\rvert < 10^{-8}$ carbaryl solutions are stable at least for a week. Kinetic constants calculated for solutions of carbaryl in 10% (v-v) ethanol-water medium are of the same order as the results obtained by Aly and El-Dib (1971) for solutions in 2% (v-v) methanol-water medium ($t_{0.5}$=15 min at pH 10).

Taking into account that micelles can be considered as differentiated phases in solution (Menger and Portnoy 1967) and the interactions between substrate with the micelle, it can be assumed that the hydrolysis reactions develop in both phases, aqueous and micellar. Thus kinetics must depend on both the concentrations of the

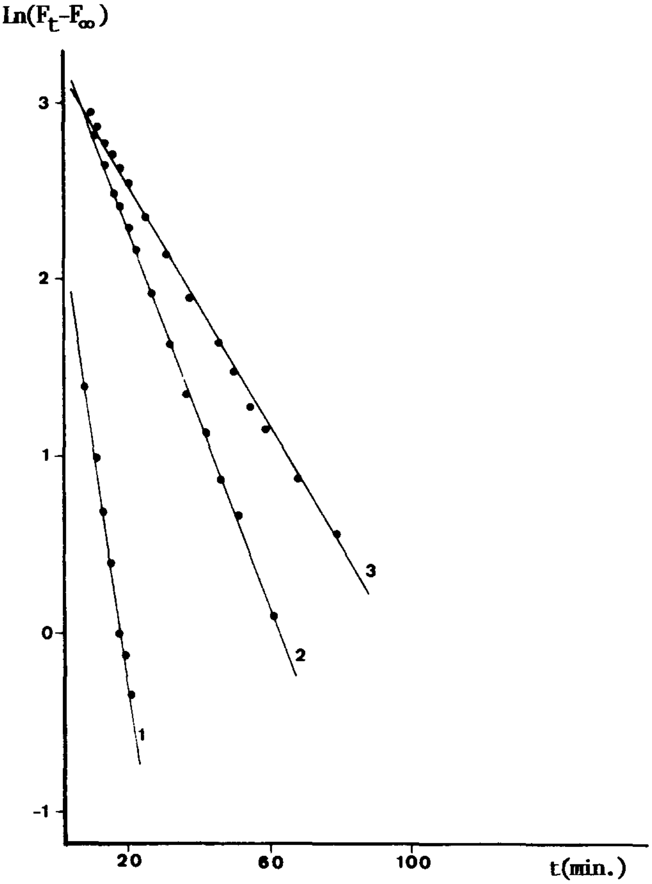

Figure 1. Variation of Ln (F_t-F_∞) versus time for the kinetics of the alkaline hydrolysis of carbaryl in micellar medium.
C_{HDTAB}=5.0•10^{-3} M, 10%(v-v) ethanol-water.
1) |OH^-|=3.2•10^{-6} M, 2) |OH^-|=5.6•10^{-6} M and
3) |OH^-|=10.0•10^{-6} M.

reagent and of the micellized surfactant (Rodenas and Vera 1985). In micellar medium, the hydrolysis reaction rate can be expressed as $V = K_\psi\ |S_T|$, where $|S_T|$ is the concentration of substratum in both phases (in micellar and aqueous phases).

After checking that 1-naphthol is photodecomposed in micellar alkaline media, the hydrolysis reaction was monitored measuring the variation of the fluorescence intensity emitted by carbaryl. From the data in Fig.1 the pseudo-first order constants (K_ψ) are calculated for every hydroxyl ion and surfactant concentration used, and plotted in Fig. 2.

The results must be explained taking into account that

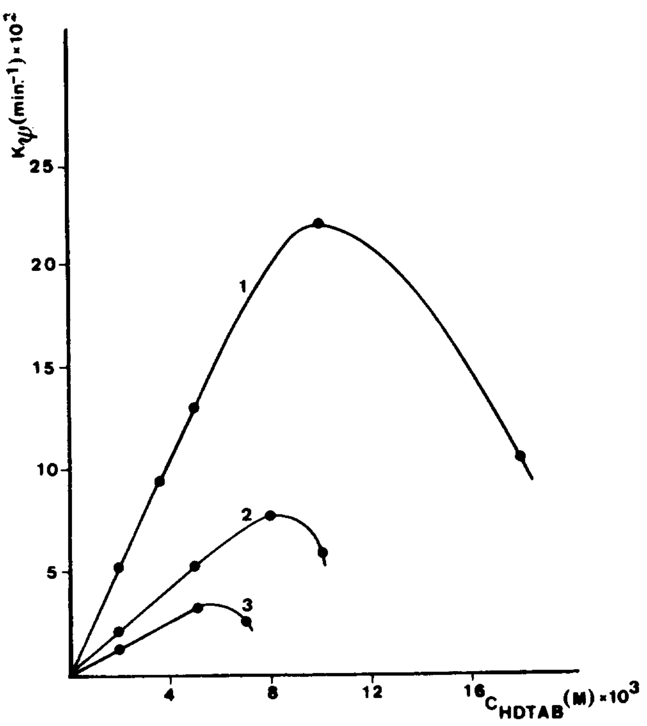

Figure 2. Variation of pseudo-first order constant versus HDTAB concentration at different pH.
1) $|OH^-|=10.0\cdot10^{-6}$ M, 2) $|OH^-|=5.6\cdot10^{-6}$ M and
3) $|OH^-|=3.2\cdot10^{-6}$ M.

in the interaction between solute with the micelle participate both electrostatic forces through the ionic head groups of the micellar surface and hydrophobic forces originated by the alkyl radicals of the surfactant. Thus, it can be accepted that for concentrations slightly higher than the critical micellar concentration, the relative concentrations of carbaryl and of hydroxyl ions in the Stern's layer increase very quickly as the surfactant concentration increases, and consequently the hydrolysis rate increases.

However, at a given concentration of surfactant, the hydroxyl ion concentration decreases with regard to the counterion (Br^-) concentration, which causes a decrease in the reaction rate. In this way an increase of the hydroxyl ion concentration in the reaction medium makes necessary a greater concentration of surfactant to reach the maximun value of the pseudo-first order constant, as can be seen in Fig.2.

Even though hydroxyl ion concentration is the main experimental factor having an influence on the hydrolysis rate of carbaryl, it may be pointed out that in the presence of cationic HDTAB micelles, the hydrolysis rate of carbaryl increases markedly, provided that the surfactant concentration does not exceed a value fixed by the hydroxyl ion concentration of the solution.

Hydrolysis rate of carbaryl in several samples of natural waters has been studied in absence and in presence of $3.0 \cdot 10^{-3}$M of the surfactant (Table 3), a concentration higher than its critical micellar concentration.

Table 3. Degradation of carbaryl in natural waters.

Samples*	(HDTAB) = 0 M		(HDATB) = $3.0 \cdot 10^{-3}$ M	
	$t_{0.5}$(hr)	$t_{0.9}$(hr)	$t^{M}_{0.5}$(hr)	$t^{M}_{0.9}$(hr)
1	138.6	-	0.72	2.18
2	28.2	583	0.67	2.88
3	44.3	-	0.14	0.90
4	16.7	120	0.13	0.42
5	9.7	-	0.12	0.32

*Describe in Table 1.

Fig.3 shows the variation of the hydrolysis rate of carbaryl as a time function, from which it is evident that the micellar system has a great influence on carbaryl hydrolysis, with $t_{0.5}/t^{M}_{0.5}$ ratios between 40 and 315 and $t_{0.9}/t^{M}_{0.9}$ ratios in the range 202-285, for those water samples where no precipitate appears during the monitoring time.

In absence of HDTAB, pH is the main factor having an influence on the hydrolysis rate. However, for sample nº 2, coming from a well near the coast which may be contaminated by sea water, the $t_{0.5}$ value calculated is lower than the calculated for sample nº 3 having a higher pH value. This result disagrees with the hypothesis of Aly and El-Dib (1971), on the basis of the results of Karinen et al. (1967) and Fukoto et al. (1967), establishing that the hydrolysis rate of carbaryl must be higher in waters with lower saline contents.

In the micellar medium, pH is also the main factor determining the hydrolysis rate. It may be considered that the lower values of $t^{M}_{0.5}$ for sample nº 2 compared with $t^{M}_{0.5}$ for sample nº 1 are abnormal. Accepting that the micelle surface selectivity by different ions in solution can be described according to an ionic exchange constant (Buton 1979; Romsted 1982), the abnormal result may be explained on the basis of the competition between hydroxyl ions and the other anions in the samples to act as counterions on the micelle surface.

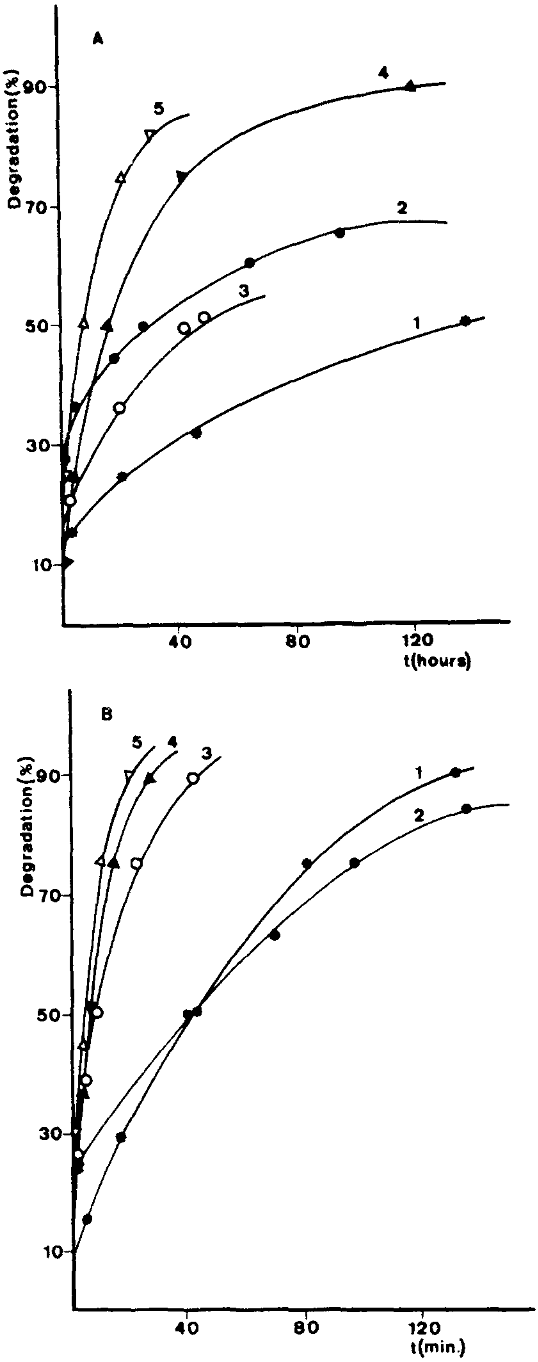

Figure 3. Degradation of carbaryl in natural waters. A.- In absence of surfactant. B.- In presence of $3.0 \cdot 10^{-3}$ M HDTAB. The samples are described in Table 1.

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