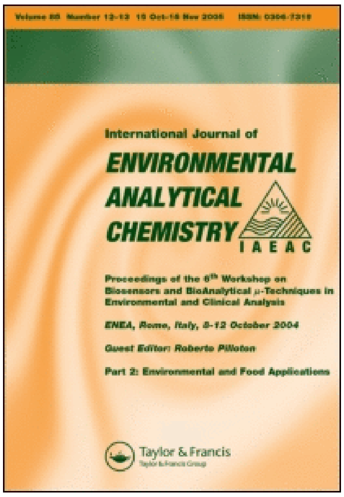

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Electron Donor–Acceptor Reagents in the Analysis of Pesticides

VII. A Simple Model System Hydrolysis of Some Cardamate Pesticides[†][‡]

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KEY WORDS: Complexing reagents, *in situ* TLC analysis, insecticide, herbicide.

The decomposition of the carbamate insecticides carbaryl and Mobam and the herbicides IPC and CIPC in water at various pH's was investigated. Analyses were performed *in situ* on silica-gel thin-layer chromatograms by reflectance spectroscopy after the developed chromatograms had been sprayed with the reagent CNTNF (9-dicyanomethylene-2,4,7-, trinitrofluorene) to form visible pi-complexes of the pesticides. Carbaryl and Mobam decomposed rapidly at basic pH's but were stable in acid. IPC and CIPC were stable in water at pH's tested.

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INTRODUCTION

The possible use of electron acceptor complexing reagents in metabolic and breakdown studies of pesticides, in conjunction with various instrumental methods of analysis, has been discussed in several papers.[1,2] The quantitative analysis of complexes *in situ* on the thin-layer chromatogram by reflectance spectroscopy has also been demonstrated.[3,4] These methods have now been applied in a study of the hydrolysis of some carbamate pesticides.

The study of the hydrolysis of the carbamates was suggested by a recent publication on the hydrolysis of organophosphorus insecticides.[5] However, the approaches to the problem and the method of analysis are quite different. In the present study, the rates of hydrolysis of two insecticidal carbamates, carbaryl and Mobam, and two herbicidal carbamates, CIPC and IPC, were investigated over a range of pH (2–9) which approximates the range of pH's found in natural waters.

The hydroxylation of carbamate pesticides has been discussed in a book by Kearney and Kaufman.[6] These compounds are known to react with water to form a variety of products.[6] The photodecomposition of some carbamate insecticides, including carbaryl, in water at various pH's upon irradiation at 254 m has also been reported.[7] Other studies have shown that carbaryl persisted longer in soil water than in lake water.[8] Recently, the hydrolysis of carbaryl under various conditions of temperature, pH and irradiation with visible light has been investigated.[9] The rate of disappearance of some common carbamate pesticides under various conditions which might be found in natural waters should therefore be of interest.

EXPERIMENTAL

Chemicals

Analytical-grade or recrystallized samples of the following pesticides were used in this study:

carbaryl: 1-naphthyl-N-methyl carbamate
CIPC: isopropyl-N-(3-chlorophenyl) carbamate (propham)
IPC: isopropyl-N-phenylcarbamate (chlorpropham)
Mobam: 4-benzothienyl-N-methylcarbamate

9-Dicyanomethylene-2,4,7-trinitrofluorene was obtained from Eastman Organic Chemicals Ltd.

The following buffers were prepared, and measured for accuracy with a Fisher Accumet Model 320 expanded scale research pH meter:

pH 2, 65 ml 0.2M HCl + 435 ml 0.2M KCl, diluted to 1 liter with distilled water;

pH 7, 22.4 ml 0.5M KH_2PO_4 + 25.8 ml 0.2M Na_2HPO_4, diluted to 1 liter with distilled water;

pH 8, 2.8 ml 0.5M KH_2PO_4 + 32.4 ml 0.5M Na_2HPO_4, diluted to 1 liter with distilled water;

pH 9, 39.8 ml 1M $NaHCO_3$ + 3.4 ml 1M Na_2CO_3, diluted to 1 liter with distilled water.

PROCEDURE

Each pesticide (25 mg) was added to 500 ml of each buffer at the various pH's in 1-liter Erlenmeyer flasks. Aliquots (50 ml) were extracted for analysis at the following time intervals: t = 0, 2 hr, 24 hr, 48 hr and 1, 2, 3, 4, 5 weeks. The flasks containing the samples were stoppered during the experiment to eliminate loss of water due to evaporation, and were kept at room temperature (20–25°C) and room lighting conditions (fluorescent lamps).

The 50-ml aliquots were adjusted to pH 2 and extracted with three 50-ml portions of ethyl ether. The extract was then washed with two 10-ml portions of distilled water, dried over anhydrous calcium sulphate and evaporated to dryness on a Büchi Rotavapour. The residue was dissolved in 2 ml of acetone which was transferred to a test tube and evaporated down to 1 ml.

ANALYSIS

Aliquots (10 mcl) of the residues were spotted on Eastman Chromagram silica-gel sheets 6061 (four samples per sheet) together with five standards of the pesticide contained in the extract at concentrations of 5, 10, 15, 20, and 25 mcg. The chromatograms were developed in an Eastman Developing Apparatus 6071 with an isopropyl ether-toluene (1:3) solvent system.[2] The developed chromatograms were dried, sprayed with a 1% solution of CNTNF in acetone and dried at room temperature. Quantitative analyses were performed on a Farrand u.v.-vis chromatogram analyzer using the reflectance mode.[3] Complexes of carbaryl-CNTNF and Mobam-CNTNF were scanned at 500 nm, IPC-CNTNF at 490 nm, and CIPC-CNTNF at 470 nm. A calibration curve was plotted for each chromatogram and the concentrations of the unknown samples were read off the plot.

RESULTS AND DISCUSSION

Both carbaryl and Mobam appeared to be quite stable in water at pH 2. As the histories of each set of samples taken at one of the times was the same, the pH 2 sample served as an internal standard against which the concentrations at the other three pH's were plotted.

The decomposition of carbaryl and Mobam at various pH's is shown in Figures 1 and 2. Both carbaryl and Mobam had disappeared in the pH 9 samples taken at 24 hr and no traces of these compounds remained at pH 8 after 1 week. At pH 7, no Mobam was found after 5 weeks, but some carbaryl was still present.

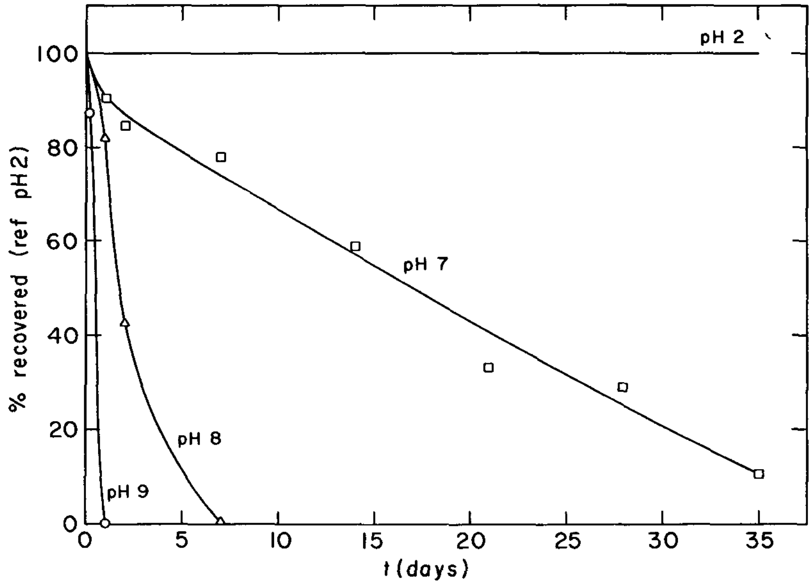

FIGURE 1 Hydrolysis of carbaryl at pH 2, 7, 8, and 9.

The appearance of the major hydrolysis products of both of these pesticides was also followed by scanning the complexes of these compounds at 500 nm simultaneously with the complexed pesticides. Their concentrations were then read off the calibration plot used for the pesticides on the same chromatogram and their concentrations were also plotted relative to the pH 2 concentration of the pesticide. The major hydrolysis product of carbaryl, which was identified as α-naphthol by measuring its u.v.-spectrum in iso-octane and in 0.4% NaOH, showed a maximum concentration at 48 hr in the pH 9 sample and had disappeared in the 1 week and subsequent samples. At pH 8, this product (H.P.1.) first appeared in the 48 hr sample, reached a maximum in the 1 week sample and had disappeared in the 5 week sample. At pH 7, this product first appeared in the 2 week sample and then began a gradual disappearance, as shown in Figure 3. A second product (H.P.2) also appeared in significant concentrations in the pH 7 and pH 8 samples in the first week of the experiment, but was not identified.

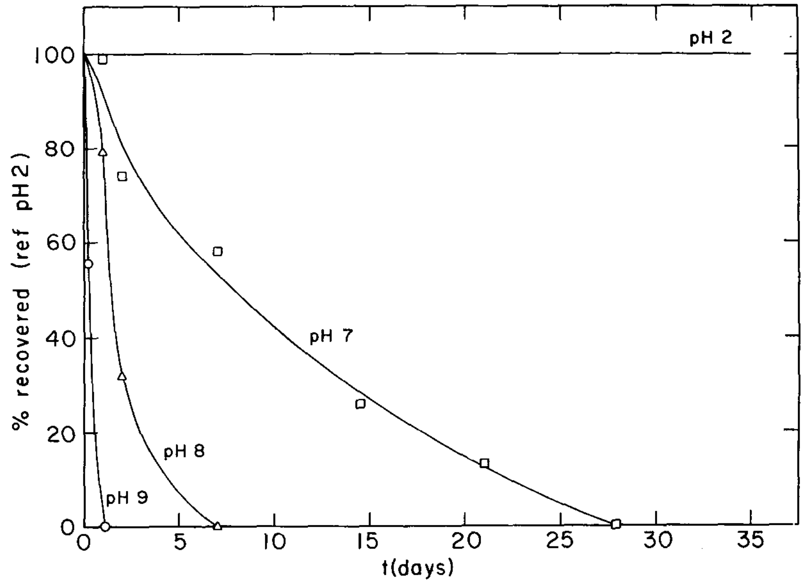

FIGURE 2 Hydrolysis of Mobam at pH 2, 7, 8, and 9.

The appearance of the major decomposition product of Mobam at the various pH's is shown in Figure 4. This product appeared at the various pH's in the same order as did the α-naphthol formed by the hydrolysis of carbaryl, but was more persistent. (No decomposition products were observed for either carbaryl or Mobam at pH 2, as previously noted.)

The herbicides IPC and CIPC appeared quite stable in water at the various pH's. Recovery rates averaged ~ 60% for all samples at all the pH's studied.

R_f's of the pesticides and major decomposition products are given in Table I.

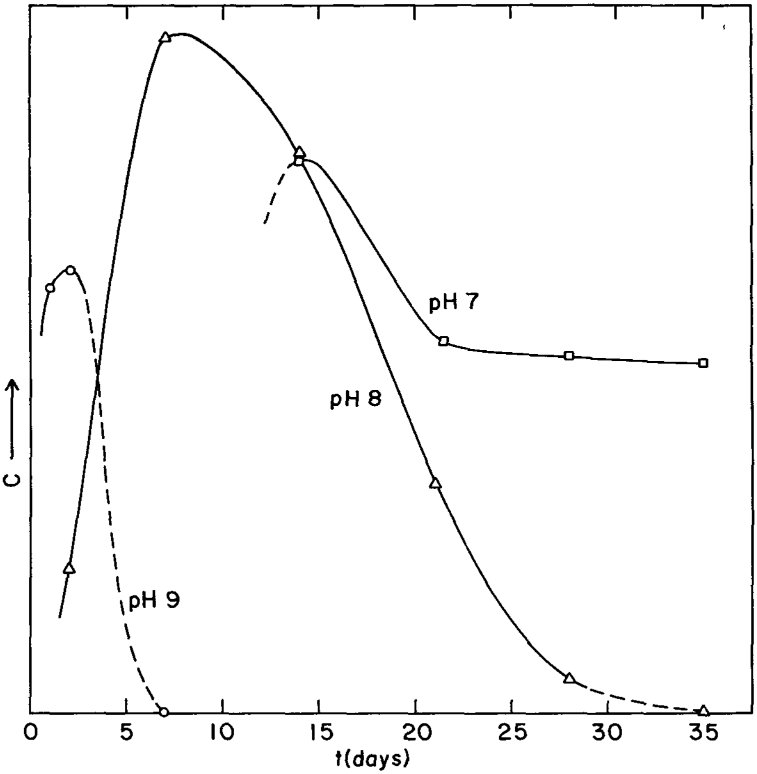

FIGURE 3 Appearance and disappearance of major hydrolysis product of carbaryl at pH 7, 8, and 9.

TABLE I

Chromatographic results for carbaryl, Mobam, and their major hydrolysis products on Chromagram sheets 6061, solvent system iso-propyl ether-toluene (1:3)

Compound	R_f
Carbaryl	0.48
Carbaryl-H.P. 1 (α-naphthol)	0.64
Carbaryl-H.P. 2	0.82
Mobam	0.46
Mobam-H.P. 1	0.75

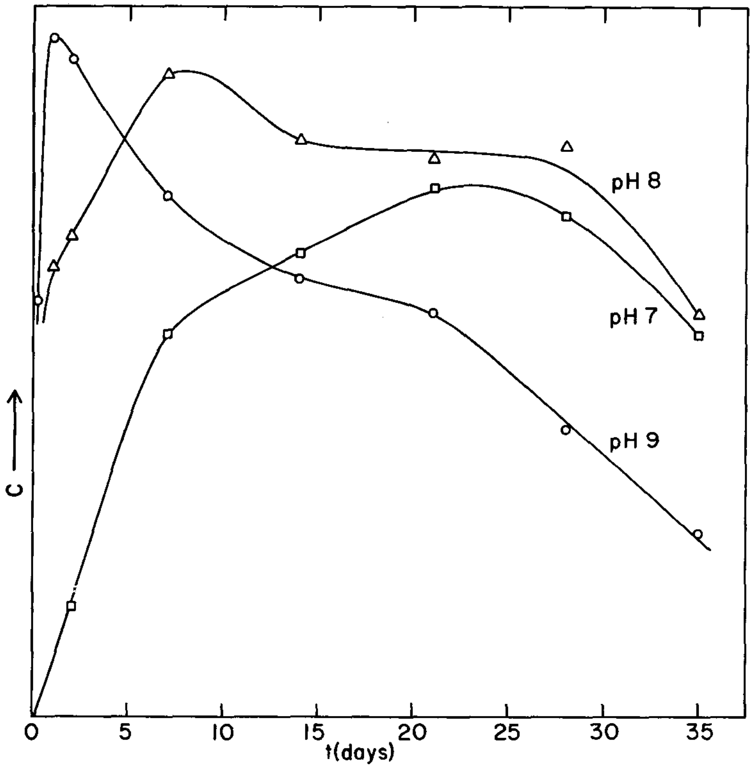

FIGURE 4 Appearance and disappearance of major hydrolysis product of Mobam at pH 7, 8, and 9.

CONCLUSIONS

The experiments indicate that the N-methyl carbamate insecticides studied decompose fairly rapidly in water at alkaline pH's and that this process occurs more rapidly as the water becomes more basic. Reaction occurs more slowly at neutral pH and the compounds appear quite stable at acid pH. Similar behaviour is observed with the major hydrolyzed products in basic media, but these appear to be more persistent than the parent pesticides. The N-phenyl carbamates studied appear to persist under both acidic and alkaline conditions. The results suggest that the persistence in water of the pesticides studied and also of their major products, as well as the many other related pesticides in common use, should be the subject of further investigation.

The method of investigation used in this study should prove very useful as a simple but versatile preliminary approach to identify possible degradation problems which could then be the subject of more sophisticated studies.

Acknowledgements

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