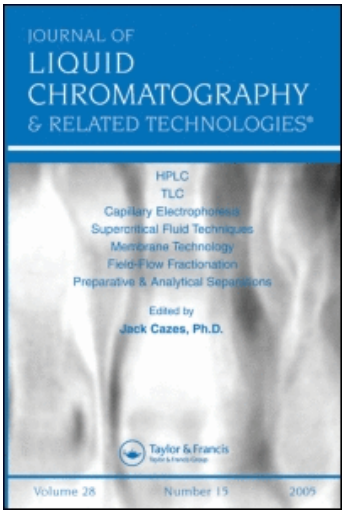

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Determination of the Ester-Cleavage Products of Some Organophosphorus Pesticides by Liquid Chromatography with Electrochemical Detection

H. B. Wan[a]; H. Chi[a]; M. K. Wong[a]; C. Y. Mok[a]; A. K. Hsieh[a]
[a] Department of Chemistry, National University of Singapore, Singapore

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DETERMINATION OF THE ESTER-CLEAVAGE PRODUCTS OF SOME ORGANOPHOSPHORUS PESTICIDES BY LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION

H. B. WAN, H. CHI, M. K. WONG,
C. Y. MOK, AND A. K. HSIEH
Department of Chemistry
National University of Singapore
Lower Kent Ridge Road
Singapore 0511

ABSTRACT

A method for determining the phenolic compounds from the hydrolysis of some organophosphorus pesticides by liquid chromatography/ electrochemical detection has been developed. A carbon fibre micro-electrode was used for the detection. Phenol, 4-nitrophenol, 3-methyl-4-nitro-phenol, and 2,4,5-trichloropyridinol in water were analyzed by the method. The responses of the four phenolic compounds increased steadily with the

increased working electrode potential within the potential range of 1.2 to 1.4 V. The detection limits were 0.1 ng for phenol, 0.5 ng for 2,4,5-trichloropyridinol, 1 ng for 4-nitrophenol, and 2 ng for 3-methyl 4-nitrophenol.

INTRODUCTION

Some organophosphorus pesticides can produce phenolic compounds through ester cleavage reactions. The determination of these compounds is very useful in studying the fate of the parent pesticides in the environment. Like other phenols, these phenolic compounds may be analyzed by colorimetry[1], gas chromatography with derivatization [2,3], or high performance liquid chromatography (HPLC) [4,5]. The HPLC method is regarded as the most suitable and convenient. Generally ultraviolet detectors are used in the method. Recently the authors developed a HPLC-UV detection method for determining the phenolic ester cleavage products and applied the method to the study on photolysis of fenitrothion in aqueous solutions (submitted for publication). In the photolysis study, simultaneous application of two or more detection methods can be very helpful in product confirmation and accurate quantification. In 1982, Shop and Mayer [6]

reported an alternative detection method which used an electrochemical detector in HPLC determination of environmental phenols at ppb level. One of the distinct advantages of the method is the ease of sample preparation and lack of interference. Water samples with concentration of phenols above $2x10^{-2}$ mg litre^{-1} can be analyzed by direct injection.

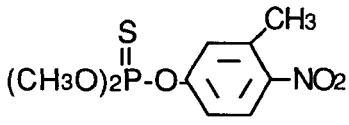
In their study, Shop and Mayer used a glassy carbon macro-electrode. During the past several years micro-electrodes have undergone rapid development. Compared with macro-electrodes, micro-electrodes have such advantages as lower iR drop, reduced charging current and enhanced mass transfer of the analytes to the electrode surfaces. Several kinds of carbon fibre electrodes have been reported for flow analysis, among which was a flexible carbon fibre flow cell which was constructed by fixing a carbon fibre into a polyethylene tube.[7,8] This kind of micro-cell is simple in structure and small in size. If the cell stops functioning properly, it is easy to change for a new fibre. Some drugs, such as nifedipine, nicardipine, pindolol[9] and salbutamol[10], in human plasma have been analyzed using this kind of electrode. In the present study, this micro-electrode

was applied to the determination of the phenolic compounds from the hydrolysis of some organophosphorus pesticides.

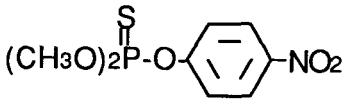
MATERIALS AND METHODS

Reagents

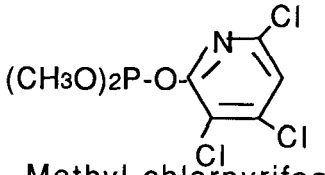
Among the phenolic compounds studied, phenol (I) and 4-nitrophenol (II) were of purity above 98%. II was also produced by hydrolyzing the organophosphorus insecticide methyl-parathion in 0.01N NaOH solution. The organophosphorus insecticide methyl-parathion, fenitrothion, and methyl-chlorpyriphos with purity above 98% were used to produce 4-nitrophenol (II), 3-methyl 4-nitrophenol (III), and 3,5,6-trichloro-2-pyridinol (IV) by hydrolysis in o.01N NaOH solution at 70-100 °C or in 0.025N NaOH solution at room temperature. The progress of the hydrolysis reactions was monitored by HPLC till the parent compounds were thoroughly hydrolyzed. HPLC-grade methanol, water (Milipore), and phosphoric acid of analytical grade were used to prepare the mobile phase. The mobile phase contained 70% of methanol , 30% of water, and 0.04% of phosphoric acid. The molecular structures of the pesticides and the phenolic compounds are as follows:



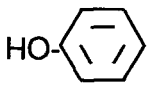
Fenitrothion



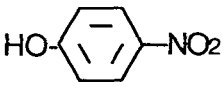
Methyl-parathion



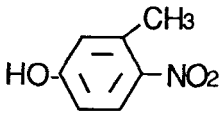
Methyl-chlorpyrifos



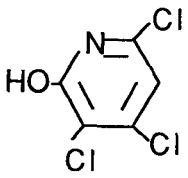
(I)



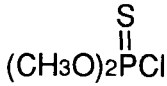
(II)



(III)



(IV)



O,O-dimethyl chlorophosphorothioate

Liquid Chromatography

A Shimadzu LC-6A liquid chromatograph equipped with a bonded octadecylsilane column (25 cm x 5 mm, ODS-3, Whatman) was used for the separation. A Waters-464 pulsed electrochemical detector was used for

amperometric detection. The HPLC column outlet was connected directly to the carbon fibre flow cell. The mobile phase flow rate was set at 0.5 ml. min^{-1}.

The carbon fibre electrode and the Ag/Ag_3PO_4 reference electrode were prepared as described previously [7]. The reference electrode was mounted downstream of the carbon fibre working electrode. A stainless steel tube (20 mm long, 1.5 mm O.D., and 0.5 mm I.D.) connected to the reference electrode was used as a counter electrode.

RESULTS AND DISCUSSION

Chromatography

Several phenols are reported to be separated on reversed phase column with the eluent containing methanol and water [4]. In the present study, solutions with different ratio of methanol to water were tested. A methanol to water ratio of 7 to 3 was used in the later experiments because under this condition the phenols studied were well separated with relatively short retention times . Addition of 0.04% of phosphoric acid to the eluent helped to inhibit the dissociation of hydrogen

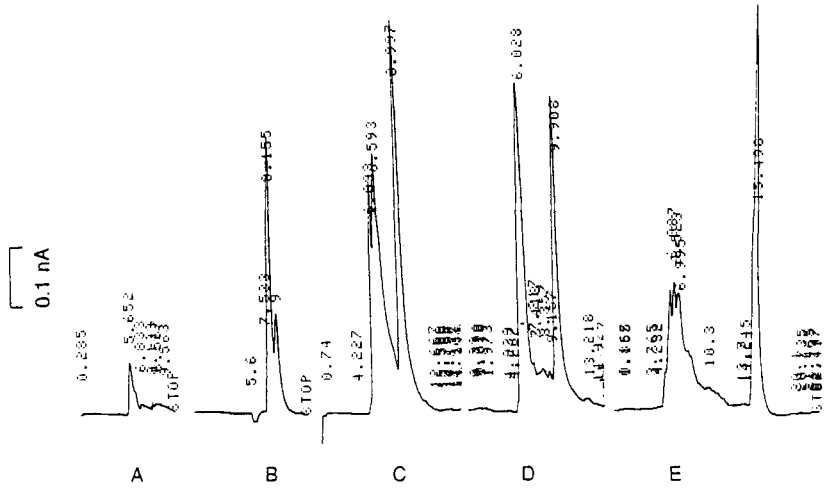
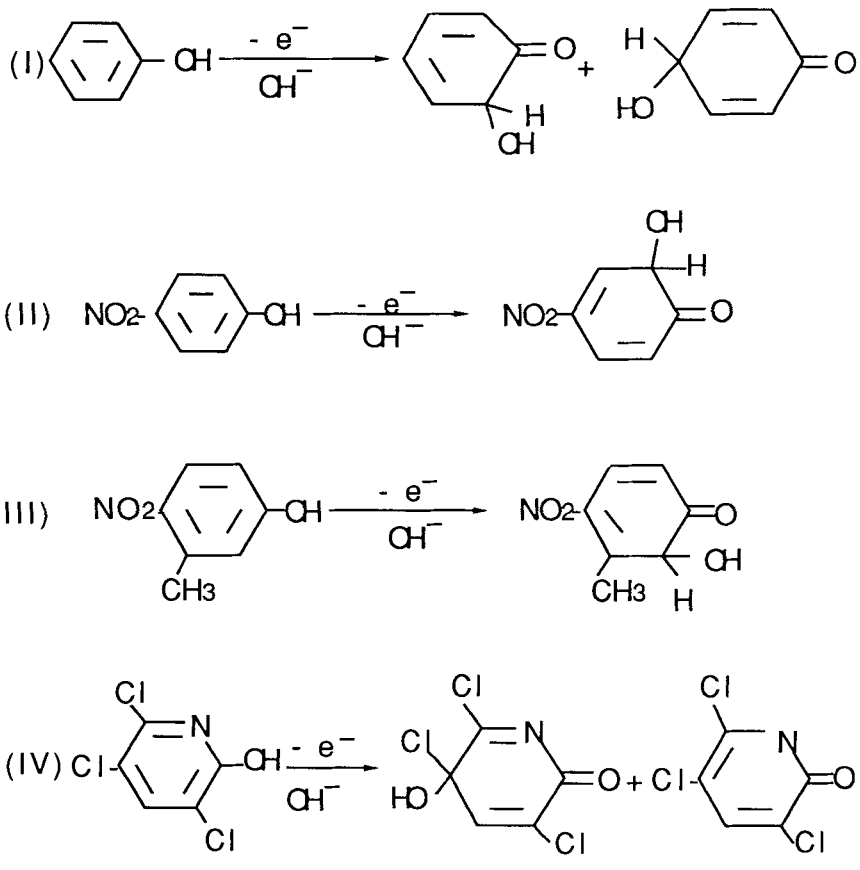


Figure 1. Chromatograms of the phenolic compounds. A. O,O-dimethyl chlorophosphorothioate (50 ng) hydrolyzed; B. I and II (30 ng each); C. II (90 ng) from hydrolyzed methyl-parathion; D.III (100 ng) from hydrolyzed fenitrothion; E. IV (80 ng) from hydrolyzed methyl-chlorpyrifos.

ion from the phenol group and thus to prevent the tailing of the chromatographic peaks. The phosphoric acid in the eluent also served as the counter ion for the silver phosphate reference electrode. The chromatograms of the phenols are shown in Figure 1 .

Hydrodynamic Voltammograms

At the working electrode, phenols are probably oxidized to their quinol forms through following processes:



In order to select the optimum working potential, hydrodynamic voltammograms for the phenols were obtained by injecting 100 ng of the phenols into HPLC with different potentials applied on the working electrode. As shown in Figure 2, the responses to the phenols increase steadily with the increase in potential

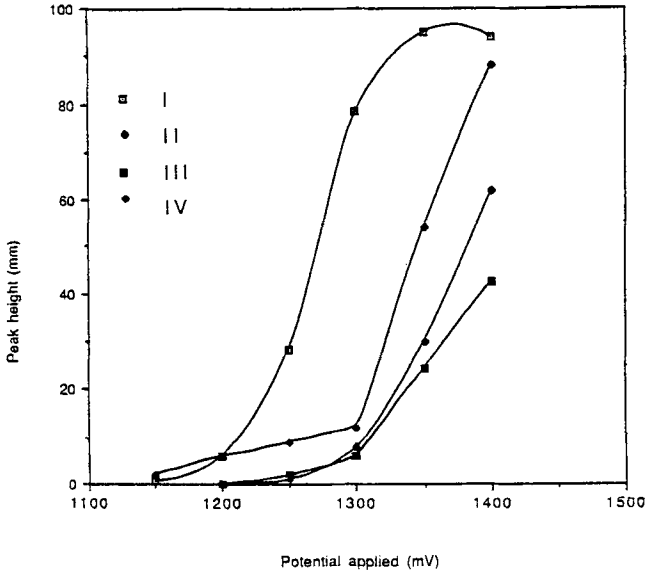


Figure 2. Responses of the phenolic compounds to the variation of the potential

within the potential range of 1.20 to 1.40 V. A potential of 1.35 V was used for later experiments as at this potential best sensitivity and signal to noise ratio were obtained. Higher potentials were not suitable for the detection because the electrode surface tends to get oxidized and increased background current with noisy baseline was observed. It can also be seen from Figure 2 that the four phenols tend to be oxidized in the order of IV> I>III>II.

Reproducibility of the Electrode Response

One of the problems with the solid electrodes is the contamination of the electrode surfaces by impurities and the oxidized products of the analytes produced by electrochemical reactions. It may cause decrease in sensitivity with the time of use. To study the reproducibility of the detection, five successive injections of a mixture containing hydrolyzed methyl-parathion, fenitrothion, and methyl-chlorpyrifos (20 ng each) were made. The relative standard deviations of the peak height were 2.9% for II, 4.5% for III, and 5.1% for IV. The results indicated that the detector sensitivity was stable during the analysis.

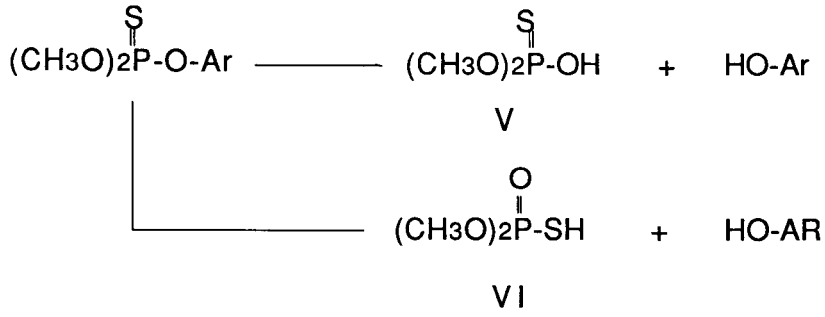
Linearity and Detection Limit

The calibration curves of the 4 phenolic compounds were obtained by injecting different amounts of the analytes into the HPLC. Within the tested range (0 t0 250 ng) there existed linear relation between the amounts of the phenolic compounds and the responses of the electrochemical detector. The square of the correlation coefficients obtained from linear regression analysis were 0.995 for I (n=5), 0.985 for II (n=5), 0.998 for III (n=4), and 0.999 for IV (n=3).

The detection limits were 0.1 ng for I, 0.5 ng for IV, 1 ng for II, and 2 ng for III with a signal/noise ratio of 5/1. If the injection volume is 20 ul, the minimum detectable concentration in water by direct injection will be $5X10^{-3}$ mg $litre^{-1}$ for I, $25x10^{-3}$ mg $litre^{-1}$ for IV, $50x10^{-3}$ mg $litre^{-1}$ for II, and $100x10^{-3}$ mg $litre^{-1}$ for III.

Determination of Other Ester-cleavage Products of Organophosphorus Pesticides

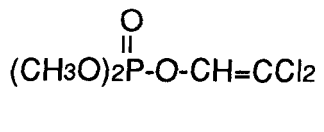
In addition to the phenolic compounds, O,O-dimethyl phosphorothioate (V) and O,O-dimethyl phosphorothioloate (VI) were also produced when the three organophosphorus pesticides were hydrolyzed [11].



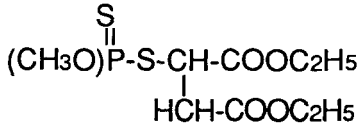
According to the study with parathion, hydrolysis in organic solvent favors the formation of VI, whereas water solution favors formation of V [11]. When O,O-

dimethyl chlorophosphorothioate was hydrolyzed in 0.01N NaOH solution, it gave a peak with retention time of 5.6 min on the chromatogram (Figure 1 A), which could be compound V. When fenitrothion was hydrolyzed in acetonitrile it gave a peak with retention time of 6.0 min (Figure 1 D). It could be compound VI. It suggests that the micro-electrode could also be used to detect the compound V and VI. Unfortunately the two peaks could not be confirmed because of lack of authentic compounds.

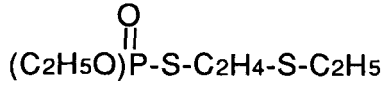
Organophosphorus pesticides dichlorvos, malathion, and Di-syston were also hydrolyzed under the conditions similar to that for fenitrothion and methyl-parathion. The hydrolyzed samples with concentration of 10 to 25 mg litre^{-1} were analyzed by this HPLC method. No response from the alchololic moeity was observed.



Dichlorvos



Malathion



Di-syston

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