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Electrochemical Study And Analysis of Captafol

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ABSTRACT

The electrochemical reduction behavior of the fungicide captafol has been studied by employing direct current polarography, cyclic voltammetry, differential pulse polarography, millicoulometry and controlled potential electrolysis. The general reduction mechanism has been suggested. Differential pulse polarographic method was used to estimate captafol in agricultural formulations. Both standard addition and calibration methods are used for the analytical experiments. The lower detection limit is found to be 1.20×10^{-9} M.

KEYWORDS

Captafol;
D.C.polarography;
Cyclic voltammetry;
Agricultural formulations.

INTRODUCTION

Captafol[N-(1,1,2,2-tetrachloro-ethylthio) cyclohex-4-ene-1,2-dicarboximide is a protective nonsystemic fungicide widely used to control foliage and fruit diseases of tomatoes, coffee berry disease, potato blight, tapping panel disease of rubber and many other diseases. It is also used in the lumber and timber industries to reduce losses from wood rot fungi in logs and wood products[1].

Determination of captafol in commercial formulations and residues on grains and apples by colorimetric method[2], captafol and other pesticides are studied in apple, Japanese pear and melon by simultaneous extraction and determined by HPLC equipped with a fluorescence detector, using capillary gas chromatographic determination of captafol in vegetables, fruits and grains[3], determination of captafol and other pesticide residues in fruits and vegetables, using gas chromatography with electron capture detection, mills procedure[4], using wide-bore capillary column gas chromatography with electron capture detection for the determination of captafol and other residues in tomatoes, cucumbers, and apples[5], a rapid analytical method for determination of pesticide residues in wines by GC-ECD with large-volume injection system[6], the residues of captafol and metalaxyl were analyzed periodically after the last application through gas liquid chromatography[7].

Electrochemical techniques[8,9] have been widely used for the determination of carbonyl containing pesticides. But, no attention has been paid to understanding the electrochemical behavior of captafol and its formulations.

The article attempts to understand the electrochemical behavior of captafol and its determination in agricultural formulations.

EXPERIMENTAL

The theoretical and the experimental procedure of these techniques were discussed elsewhere[10]. All the chemicals used were of analytical grade. Pure captafol was obtained from 'Promochem', Germany. The purity of the compound was tested by melting point determination. Stock solution was prepare by dissolving the required amount of the compound in dimethylformamide. Universal buffers of pH range 2.0 to 12.0 were prepared using 0.2M boric acid. 0.5M citric acid and 0.1M trisodium orthophosphate[11].

RESULTS AND DISCUSSION

Captafol was found to give a single well define wave/peak in acidic solution($2 \leq pH \leq 6$) which is attributed to the simultaneous reduction of the two carbonyl groups to the corresponding hydroxyl derivative in a four-electron process. No reduction is observed in the basic medium($8 \leq pH \leq 12$) due to the precipitation of the electroactive species.

The diffusion controlled nature of the electrode process is evidenced from the linear plots of i_d versus $h^{1/2}$ and i_m versus $t^{2/3}$ that pass through the origin indicating the absence of adsorption complications[12]. The experimental constancy of $i_p/1/2$ CV with scan rate(V) has shown the electrode process to be free from any kinetic complications. Conventional log-plot analysis and the variations of $E_{1/2}$ E_p and E_m (where E_m is the potential at maximum current in differential pulse polarography) values towards more negative potentials upon increasing the concentration of captafol[13] indicated the irreversibility of the electrode process. Typical voltammograms for captafol are shown in figures 1 and 2.

Millicoulometry employed at pH 2.0 to find out the number of electrons involved in the electrode process. The results showed the number of electrons to be four. From the slope of the $E_{1/2}$ vs. pH plot, the number of protons involved in the rate determining step of the electrode process is found to be two. Controlled potential electrolysis experiments were carried out at -0.27 V vs saturated calomel electrode in pH 4.0. The isolated product was identified as hydroxyl product and confirmed by IR spectrometry (3500 to 3200 cm^{-1}; nujol medium).

Based on the results obtained, the electrochemical reduction mechanism of captafol can be proposed as in SCHEME 1.

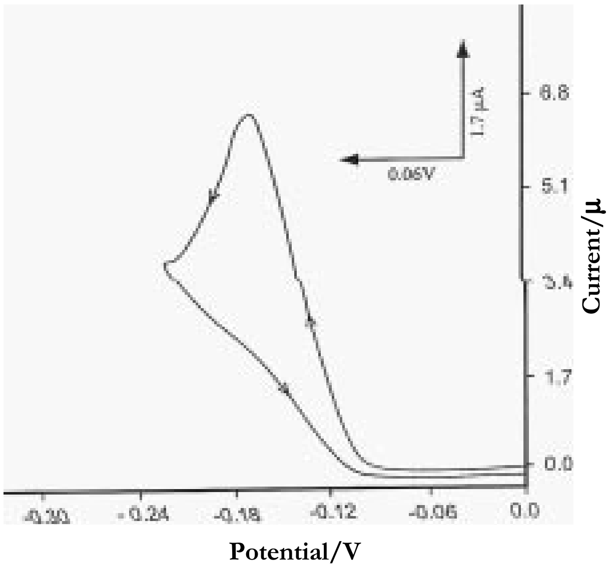


Figure 1: Typical differential pulse polarogram of captafol in pH 4.0

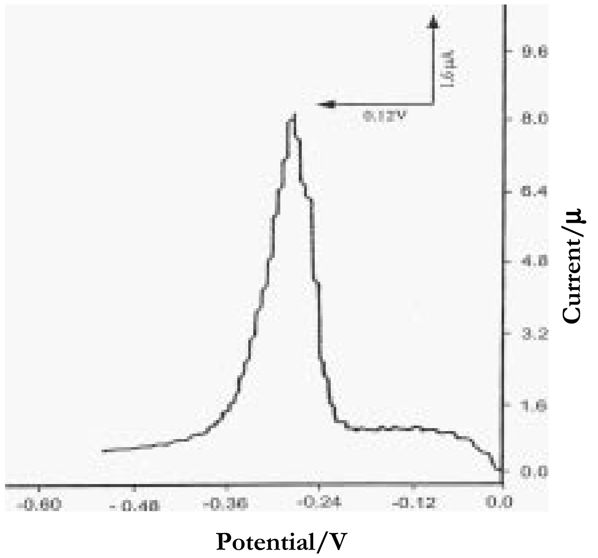
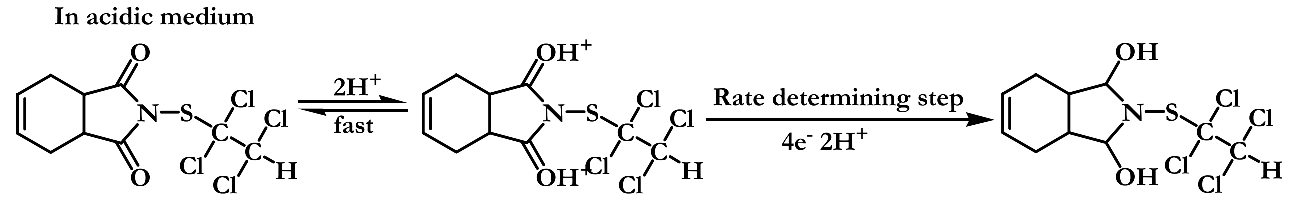


Figure 2: Typical cyclic voltammogram of captafol in pH 2.0



SCHEME 1

Procedure

Differential pulse polarographic peak obtained in pH 4.0 was used in the analytical estimation of captafol. Standard addition and calibration methods were used for the analysis of the captafol. The peak current was found to vary linearly with the captafol concentration over the range of 1.5×10^{-5} to 1.2×10^{-9} M. The lower detection limit was calculated using the expression[14] dl=3×Sd/m where Sd is the standard deviation and m, the slope of the calibration plot.

Analytical procedure

Captafol is analyzed by the standard addition method. The standard solution(1×10^{-5} M) is prepared by dissolving the appropriate amount of the electro active species in dimethylformamide. One ml of the standard solution is transferred to the polarographic cell and made up to 10ml with the supporting electrolyte to get the required concentration and then deoxygenated by bubbling nitrogen gas for 10min. After recording the polarogram, small increments of the standard solutions(05.ml) were added and then polarograms were recorded for each addition under similar conditions. The optimum conditions for the determination of captafol in pH 4.0 were found to be a drop time of sec, pulse amplitude of 50 mV, and an applied potential of -0.27 V vs saturated calomel electrode.

The relative standard deviation and correlation coefficient values were found to be 1.64 and 0.9423 respectively, for 10 replicates. The described analytical procedure is used the determination of captafol in its formulation(captofol).

Application

The required quantity of captafol formulation corresponding to a stock solution 1×10^{-3} M was accurate measured and transferred into a 100ml calibrated flask containing 50ml dimethylformamide. A solution is approximately 1×10^{-5} M was prepared by dilution of stock solution with pH 4.0. The assay results for captafol in formulation in pH 4.0 are given in TABLE 1.

TABLE 1: Determination of captafol in pure and formulation by differential pulse polarography

Compound	Labelled amount (mg)	Amount* found (mg)	Recovery (%)	Standard deviation
Captafol (pure)	5.0	4.955	99.10	0.011
	10.0	9.952	99.52	0.012
	20.0	19.95	99.75	0.014
	25.0	24.685	98.74	0.020
	30.0	29.645	98.88	0.051
Captafol formulation				
Captafol (captofol)	5.0	4.948	98.96	0.025
	20.0	19.95	99.75	0.013
	25.0	24.95	99.42	0.007
	30.0	29.975	99.16	0.012

* Average of five determinations

Recovery of captafol ranging from 98.74 to 99.75 obtained with the proposed differential pulse polarogram method indicates its accuracy and reproducibility.

The proposed method is simple, rapid, reliable and sensitive and does not involve the elaborate clean-up procedure required by the other methods. Hence the development method can be used in fungicidal formulations.

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