



Trade Science Inc.

ISSN: 0974 - 7516

Volume 7 Issue 1

Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 7(1), 2011 [26-29]

Electrochemical reduction behaviour of chlomethoxyfen

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Received: 10th June, 2010 ; Accepted: 20th June, 2010

ABSTRACT

The electrochemical reduction behaviour of chlomethoxyfen has been studied using d.c. polarography, cyclic voltammetry, millicoulometry and controlled potential electrolysis in universal buffers of pH values ranging from 2.0 to 12.0 in double distilled-water. Kinetic parameters such as diffusion coefficient (D) and heterogeneous forward rate constant ($K_{f,h}^{\circ}$) values are evaluated and reported. A reduction mechanism is proposed in consistence with the data obtained. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Chlomethoxyfen;
d.c.polarography;
Cyclic voltammetry;
Millicoulometry;
Controlled potential
electrolysis.

INTRODUCTION

There are increasing kinds of chemical substances in the environment that cause large social problems. Several hundred various pesticides are soiled worldwide in agricultural production, among these chlomethoxyfen [5-(2,4-dichlorophenoxy)-2-nitroanisole] (Figure 1) is one of the important and a potent herbicide^[1,2], which is effective against many annual weeds and some perennials^[2]. Pesticides runoff from agricultural lands impacts the water environment^[3,5] and some of the pesticides are endocrine disrupting compounds^[6,7]. Therefore, it is necessary to limit the chemical substances discharged into the environment as much as possible, and also to remove them as completely as possible. To remove pesticides from water in the environment, photochemical decomposition by ultraviolet irradiation^[8], ozonation^[9] or alkaline hydrolysis^[10,11] have usually been used.

Very little attention has been paid to the electrochemical study of this compound. This work elucidates

the electrochemical behaviour of chlomethoxyfen by using d.c. polarography and cyclic voltammetry.

EXPERIMENTAL

A PARK Model 364 polarographic analyzer coupled with BD 8 Kipp and Zonen x-t recorder was used for d.c. polarographic measurements. Cyclic voltammetric experiments were performed using Meterohm E-506 polarecord coupled with E-612 VA-scanner, E-648 VA controller and a digital electronics 2000 X-Y/t recorder. All electrochemical measurements were carried out using a conventional three electrode design at 298K, The dropping mercury electrode (with an area of 0.0223 cm² and flow rate of 2.73 mg s⁻¹) and hanging mercury drop electrode (with an area of 0.0328

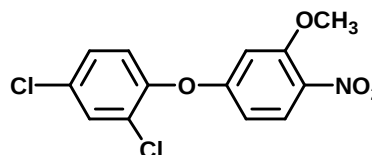


Figure 1 : Chemical structure of chlomethoxyfen

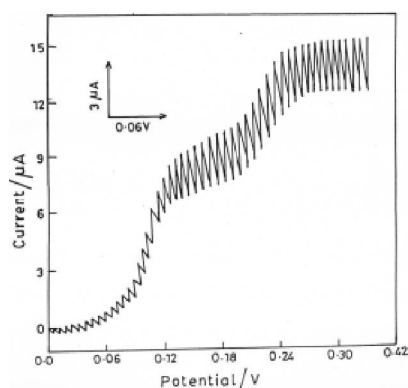


Figure 2 : Typical d.c.polarogram of chlomethoxyfen in pH 2.0, concentration: 0.5 mM, drop time: 3Sec

TABLE 1 : Typical d.c. polarographic data of flumetralin, concentration: 0.5mM, drop time: 3s

pH	$-E_{1/2}/V$	$I_d/\mu A$	Δn_a	$D \times 10^6 / cm^2 s^{-1}$	$K^\circ_{f.h.} / cm s^{-1}$
2.0	a) 0.10	9.0	0.84	9.28	1.86×10^{-4}
	b) 0.23	4.0	0.48	3.20	2.02×10^{-5}
4.0	a) 0.27	8.7	0.82	8.90	2.14×10^{-5}
	b) 0.38	3.8	0.39	2.91	6.06×10^{-6}
6.0	a) 0.41	8.3	0.84	8.60	2.90×10^{-8}
	b) 0.52	3.0	0.44	2.68	4.06×10^{-9}
8.0	0.56	7.7	0.75	7.60	4.20×10^{-10}
10.0	0.70	7.5	0.81	7.12	9.90×10^{-12}
12.0	0.85	7.1	0.80	6.40	3.64×10^{-14}

a) first peak, b) second peak

cm^2) were used as working electrode (SCE) for d.c. polarography. A platinum counter electrode was used for the above techniques to complete the electrolytic circuit. A modified cell, with mercury pool cathode, SCE platinum (with an area of $0.03022 cm^2$) wire gauze electrode and spot galvanometer, was used for controlled potential electrolysis.

Pure chlomethoxyfen was obtained from Hindustan Ciba-Geigy Ltd., Bombay and was used without further purification. Universal buffers of pH 2.0-12.0 were prepared by using 0.1M boric acid, 0.05M citric acid and 0.1M trisodium orthophosphate. All chemicals used were of pure analytic grade. Stock solution was prepared by dissolving the required amount of chlomethoxyfen in double distilled water and making up with the supporting electrolyte to obtain the desired concentration. The test solution was purged with purified nitrogen gas for 10 minutes before the voltammograms were taken. 0.02% aqueous solution of Triton X-100 was used to eliminate the polarographic maxima encountered throughout the polarogram.

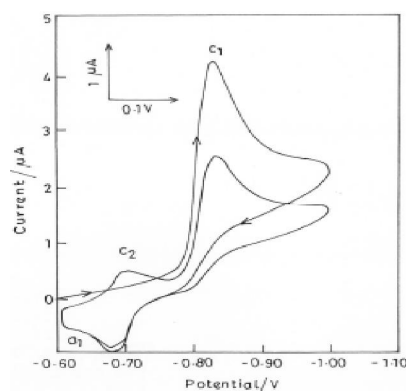


Figure 3 : Typical cyclic voltammogram of chlomethoxyfen in pH 12.0, concentration: 0.5mM, scan rate: $40 mVs^{-1}$

TABLE 2 : Typical cyclic voltammetric data of flumetralin, concentration: 0.5 mM, scan rate: $40 mVs^{-1}$

pH	$-E_p/V$	$I_p/\mu A$	Δn_a	$D \times 10^6 / cm^2 s^{-1}$	$K^\circ_{f.h.} / cm s^{-1}$
2.0	a) 0.10	7.1	0.85	9.01	1.70×10^{-4}
	b) 0.26	3.6	0.51	3.62	3.26×10^{-5}
4.0	a) 0.26	6.4	0.75	8.60	2.56×10^{-6}
	b) 0.43	3.1	0.42	3.53	6.86×10^{-7}
6.0	a) 0.41	5.8	0.82	8.20	6.32×10^{-8}
	b) 0.55	2.6	0.43	3.41	6.26×10^{-9}
8.0	0.57	5.2	0.71	7.70	4.82×10^{-10}
10.0	0.72	4.7	0.82	7.74	8.30×10^{-13}
12.0	0.84	4.3	0.79	7.10	2.10×10^{-17}

a) first peak, b) second peak

RESULTS AND DISCUSSION

Chlomethoxyfen is found to give two well resolved waves/peaks in the pH range 2.0 to 6.0. The first waves/peaks are found to be due to the reduction of the nitro group to hydroxylamine in a four electron process and the second to the reduction of the hydroxylamine to amine in a two electron process. The waves/peaks height ratios are found to be 2:1. However, in alkaline solutions (pH 8.0 to 12.0) the title compound exhibits only a four electron waves/peaks which corresponds to the reduction of the nitro group to hydroxylamine. In the alkaline medium, hydroxylamine is not reduced further to amine owing to the non-availability of protons. Typical voltammograms are shown in figure 2 and 3.

In Cyclic voltammetric experiments, a small anodic peak (a_1) has been observed in the reverse scan at higher pH values ($pH \geq 10$) as shown in figure 3. In the second scan, another small cathodic peak (c_2) at more positive potentials than c_1 is noticed. The anodic peak

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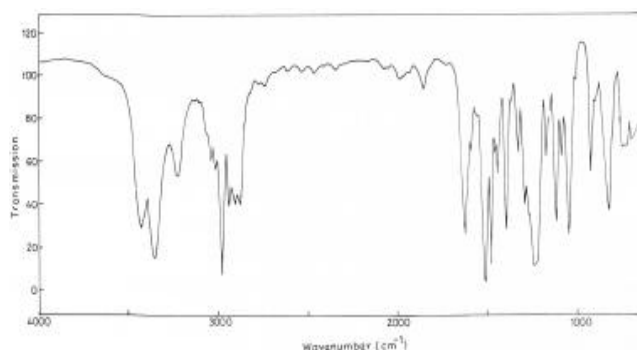


Figure 4 : I.R.spectrum of the reduction product of chlomethoxyfen

(a_1) may be attributed to the oxidation of reduced product at c_1 ($R-NHOH \rightarrow R-NO + 2e^- + 2H^+$) and the cathodic peak (c_2) to the reduction of the oxidised product at a_1 ($R-NO + 2e^- + 2H^+ \rightarrow R-NHOH$). This redox couple is noticed to be irreversible as evidenced by the separation of their E_p values.

The diffusion controlled and absorption free nature of the electrode from the linear plots of i_d vs $h^{1/2}$ and i_p vs $v^{1/2}$ passing through origin. In cyclic voltammetry, the current function $i_p/Cv^{1/2}$ is found to be fairly constant with scan rate (v) also indicating the electrode processes to be free from kinetic complications. The irreversible nature of the wave (s) is confirmed by logarithmic plots^[12] and for each reduction process E_{dc} is plotted against $[\log i/(i_d - i) - 0.546 \log t]$ and it is found to be appreciably exceeding $54.2/n$ mV. Further the fact that $E_{1/2}$ and E_p are observed to be shifted towards more negative values with increasing concentration of chlomethoxyfen indicated the irreversible nature of the electrode process^[9]. The irreversibility is also indicated by the variation of peak potential (E_p) with scan rate (v) in cyclic voltammetry.

The reduction potentials of the chlomethoxyfen peaks are found to be dependent on pH and found to shift towards more negative potentials with increase in pH of the buffer solutions indicating the proton involvement in the electrode process. From the equation^[12].

$$\frac{dE_{1/2}}{dpH} = \frac{-0.05915}{\alpha n_a}$$

where, p = number of protons involved in the rate determining step

n_a = number of electrons involved in the rate determining step

α = transfer coefficient

p , for the reduction of nitro group is found to be one. The αn_a values for the reduction of nitro group are found to be in the range of 0.86-0.98 indicating that two electrons take part in the rate determine step^[12,13]. A similar stoichiometry of rate determining step for the reduction of nitro group has been reported^[14].

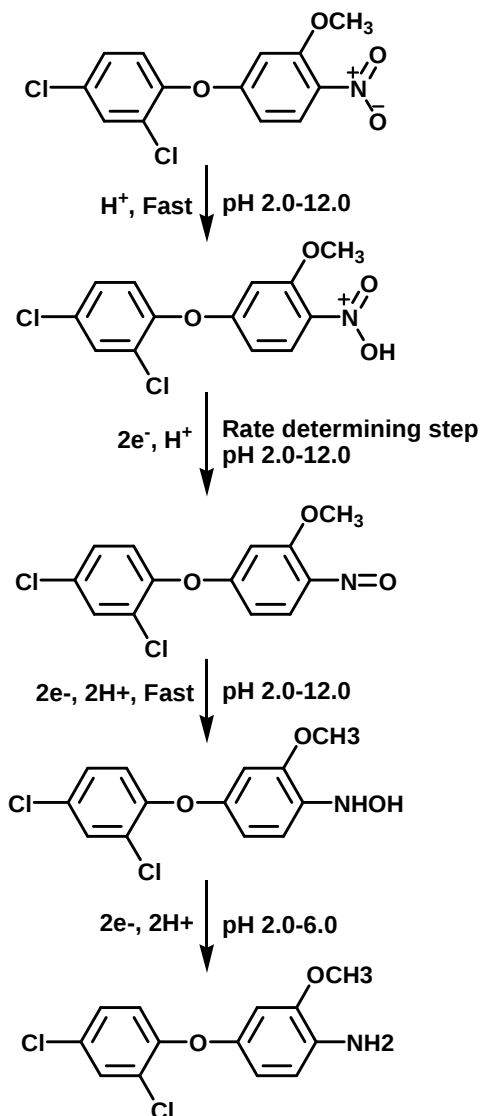
The number of electrons involved in the reduction process is calculated from the results obtained with millicoulometry. In pH 2.0, the 'n' is found to be four and two for the first and second waves respectively. In pH 12.0 only four-electron addition is indicated. Hence, the reduction product of chlomethoxyfen in basic media is likely to be hydroxylamine. The formulation of hydroxylamine is also evidenced from cyclic voltammetric measurements, where it underwent further oxidation to a nitroso derivative in the reverse scan with an appearance of a new anodic peak. The nitroso-hydroxylamine is the ultimate reduction product. The same results are obtained through controlled potential electrolysis (CPE) experiments. Control potential electrolysis is carried out in pH 2.0 and 12.0 at -0.25 V and -0.90 V vs. SCE and the products are identified as corresponding amine (N-H stretch: 3425 cm^{-1} , 3355 cm^{-1} and N-H bend: 1625 cm^{-1} (Figure 4)) and hydroxylamine respectively through I.R. spectral data.

The typical kinetic parameters of the electrode process evaluated from d.c. polarography and cyclic voltammetry are reported in TABLE 1 and 2. The variation of diffusion current and peak current with the pH of the supporting electrolyte influences the diffusion coefficient values also to vary in the same manner. The reason for slight decrease in D values with increase in pH may be attributed to the less availability of protons with increase in pH. The diffusion coefficient values obtained from the two techniques are seen to be in good agreement due to the adsorption free nature of the electrode process.

The heterogeneous forward rate constant values (K_{fh}°) obtained for the reduction of nitro group in acidic medium from the two techniques are found to be high indicating that the rate of reaction is fast in acidic solutions due to the fact that the involvement of protons is high. In basic medium, the reduction process does not easily occur owing to the less availability of protons. Therefore, lower rate constant values are obtained.

Based on the results obtained, the electrochemical

reduction behaviour of chlomethoxyfen can be proposed as follows:



Scheme 1 : The electrochemical reduction behaviour of chlomethoxyfen

ACKNOWLEDGEMENT

The author (KB) thanks for UGC [No.F.31-24 (SC) 2007 (SA-III)], New Delhi for providing Post Doctoral Fellowship.

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