Electrochemical reduction behaviour of chlomethoxyfen

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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 (K²f.h) values are evaluated and reported. A reduction mechanism is proposed in consistence with the data obtained.

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 herbicide¹¹,²¹, which is effective against many annual weeds and some perennials²¹. Pesticides runoff from agricultural lands impacts the water environment¹³,²³ and some of the pesticides are endocrine disrupting compounds⁶,⁷. 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 irradiation⁸, ozonation⁹ or alkaline hydrolysis¹⁰,¹¹ 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 Metrohm E-506 polarecord coupled with E-612 VAscanner, 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 mgs⁻¹) and hanging mercury drop electrode (with an area of 0.0328
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 trusodium 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.

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

<table>
<thead>
<tr>
<th>pH</th>
<th>$E_{1/2}$/V</th>
<th>$I_p$/µA</th>
<th>$\Delta n_m$</th>
<th>$\Delta x$/cm$^2$ s$^{-1}$</th>
<th>$K_{ie}$/ cm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>a) 0.10</td>
<td>9.0</td>
<td>0.84</td>
<td>9.28</td>
<td>$1.86\times10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>b) 0.23</td>
<td>4.0</td>
<td>0.48</td>
<td>3.20</td>
<td>$2.02\times10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>a) 0.27</td>
<td>8.7</td>
<td>0.82</td>
<td>8.90</td>
<td>$2.14\times10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>b) 0.38</td>
<td>3.8</td>
<td>0.39</td>
<td>2.91</td>
<td>$6.06\times10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>a) 0.41</td>
<td>8.3</td>
<td>0.84</td>
<td>8.60</td>
<td>$2.90\times10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>b) 0.52</td>
<td>3.0</td>
<td>0.44</td>
<td>2.68</td>
<td>$4.06\times10^{-9}$</td>
</tr>
<tr>
<td>8.0</td>
<td>0.56</td>
<td>7.7</td>
<td>0.75</td>
<td>7.60</td>
<td>$4.20\times10^{-10}$</td>
</tr>
<tr>
<td>10.0</td>
<td>0.70</td>
<td>7.5</td>
<td>0.81</td>
<td>7.12</td>
<td>$9.90\times10^{-12}$</td>
</tr>
<tr>
<td>12.0</td>
<td>0.85</td>
<td>7.1</td>
<td>0.80</td>
<td>6.40</td>
<td>$3.64\times10^{-14}$</td>
</tr>
</tbody>
</table>

a) first peak, b) second peak

**Table 2:** Typical cyclic voltammetric data of flumetralin, concentration: 0.5 mM, scan rate: 40 mV s$^{-1}$

<table>
<thead>
<tr>
<th>pH</th>
<th>$-E_p$/V</th>
<th>$I_p$/µA</th>
<th>$\Delta n_m$</th>
<th>$\Delta x$/cm$^2$ s$^{-1}$</th>
<th>$K_{ie}$/ cm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>a) 0.10</td>
<td>7.1</td>
<td>0.85</td>
<td>9.01</td>
<td>$1.70\times10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>b) 0.26</td>
<td>3.6</td>
<td>0.51</td>
<td>3.62</td>
<td>$3.26\times10^{-5}$</td>
</tr>
<tr>
<td>4.0</td>
<td>a) 0.26</td>
<td>6.4</td>
<td>0.75</td>
<td>8.60</td>
<td>$2.56\times10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>b) 0.43</td>
<td>3.1</td>
<td>0.42</td>
<td>3.53</td>
<td>$6.86\times10^{-7}$</td>
</tr>
<tr>
<td>6.0</td>
<td>a) 0.41</td>
<td>5.8</td>
<td>0.82</td>
<td>8.20</td>
<td>$6.32\times10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>b) 0.55</td>
<td>2.6</td>
<td>0.43</td>
<td>3.41</td>
<td>$6.26\times10^{-9}$</td>
</tr>
<tr>
<td>8.0</td>
<td>0.57</td>
<td>5.2</td>
<td>0.71</td>
<td>7.70</td>
<td>$4.82\times10^{-10}$</td>
</tr>
<tr>
<td>10.0</td>
<td>0.72</td>
<td>4.7</td>
<td>0.82</td>
<td>7.74</td>
<td>$8.30\times10^{-13}$</td>
</tr>
<tr>
<td>12.0</td>
<td>0.84</td>
<td>4.3</td>
<td>0.79</td>
<td>7.10</td>
<td>$2.10\times10^{-17}$</td>
</tr>
</tbody>
</table>

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 ≥ 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

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

**Figure 3:** Typical cyclic voltammogram of chlomethoxyfen in pH 12.0, concentration: 0.5 mM, scan rate: 40 mV s$^{-1}$
(a₁) may be attributed to the oxidation of reduced product at c₁ (R-NHOH → R-NO + 2e⁻ + 2H⁺) and the cathodic peak (c₂) to the reduction of the oxidised product at a₁ (R-NO + 2e⁻ + 2H⁺ → 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 v^{1/2} and i_p vs v^{1/2} passing through origin. In cyclic voltammetry, the current function i/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],

\[
\frac{dE_{1/2}}{d\text{pH}} = -\frac{0.05915}{an_a}
\]

where, p = number of protons involved in the rate determining step
n = number of electrons involved in the rate determining step
α = transfer coefficient

\[\frac{dE_{1/2}}{d\text{pH}} = -\frac{0.05915}{an_a}\]

The heterogeneous forward rate constant values (K°f.h.) obtained for the reduction of nitro group in acidic medium from the tow 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...
The reduction behaviour of chlomethoxyfen can be proposed as follows:

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{OCH}_3 \\
\text{N} & \quad \text{OH} \\
\end{align*}
\]

\[\text{H}^+, \text{Fast} \quad \text{pH} \ 2.0-12.0\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{OCH}_3 \\
\text{N} & \quad \text{OH} \\
\end{align*}
\]

\[2\text{e}^-, \text{H}^+ \quad \text{Rate determining step} \quad \text{pH} \ 2.0-12.0\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{NH}_2 \\
\end{align*}
\]

\[2\text{e}^-, 2\text{H}^+, \text{Fast} \quad \text{pH} \ 2.0-12.0\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{NH}_2 \\
\end{align*}
\]

\[2\text{e}^-, 2\text{H}^+ \quad \text{pH} \ 2.0-6.0\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{NH}_2 \\
\end{align*}
\]

Scheme 1: The electrochemical reduction behaviour of chlomethoxyfen

ACKNOWLEDGEMENT

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REFERENCES