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Electrochemical Behaviour of 3, 4-Dichlorobenzophenone Oxime

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The electrochemical reduction behaviour of 3, 4-dichlorobenzophenone oxime has been studied in different supporting electrolytes covering a pH range from 2.0 to 12.0 in methanol-water mixtures by employing d.c. polarography, cyclic voltammetry, millicoulometry and controlled potential electrolysis. The kinetic parameters such as diffusion coefficient (D) and heterogeneous forward rate constant (k^0_{f}, h) values were evaluated and reported. A reduction mechanism is proposed in consistence with the data obtained.

INTRODUCTION

Compounds with molecules containing the azomethine grouping have been known for a very long time and continually attract attention owing to the great possibilities they offer in syntheses and for practical purposes. Among the azomethine compounds the greatest attention of electrochemists has for a long time been attracted to oximes[1-6]. Most oximes are reducible in acid solution, while only a few get reduced in alkaline medium; polarographic data prove that protonated oxime gets reduced in acid and neutral solutions[1]. Controlled potential reductions of oximes in acid solution at mercury cathodes yield the amine in a four electron reduction[1,7].

The present investigation is devoted to the d.c. polarographic and cyclic voltammetric studies in order to understand the reduction behaviour of 3, 4-dichlorobenzophenone oxime in different supporting electrolytes such as Clarks and Lubs buffer (pH 2), acetate buffer (pH 4), citrate buffer (pH 6) phosphate buffer (pH 8), carbonate buffer (pH 10) and Bates and Bower buffer (pH 12), taken in methanol–water mixtures. The results obtained were used to evaluate the kinetic parameters such as diffusion coefficient and rate constant values and to ascertain the mechanism for the reduction of the oxime group in the above mentioned supporting electrolytes.

EXPERIMENTAL

3,4-Dichlorobenzophenone oxime has been prepared following the procedure given in the literature[8]. The purity of the compound was checked by melting point determination. The m.pt. of the above oxime was found to be 153°C (Lit value 153–4°)[9]. Polarographic assays were performed using Model–364 polarographic analyser coupled with Kipp and Zonen $X-Y/t$ recorder. The three electrode system comprising a DME working electrode with a drop time of 3 sec, a platinum wire auxiliary electrode and saturated calomel electrode (SCE) as reference electrode was used. Cyclic voltammetric experiments were performed using Metrohm E–506 polarecord coupled with a digital electronics 2000 $X-Y/t$ recorder. A three electrode assembly was used for all measurements. Hanging mercury drop electrode (HMDE) was employed as working electrode, a Ag/AgCl/KCl as the reference electrode and a platinum coil as the counter electrode. Voltammograms were recorded at scan rates between 40 and 800 mVs^{-1}.

A stock solution (1.0×10^{-2} M) of 3,4-dichlorobenzophenone oxime was prepared in 40% methanol. The different supporting electrolytes were prepared in double distilled water using analaR grade chemicals. Aliquots of the stock solutions were diluted with the supporting electrolyte and de-oxygenated with oxygen-free nitrogen. Elico Model LI-120 digital pH meter was used for pH measurements. All the measurements were performed at 27 ± 0.1°C.

RESULTS AND DISCUSSIONS

3,4-Dichlorobenzophenone oxime is found to be reduced in one step in all the supporting electrolytes and in both the techniques employed in the present investigation. This step may be attributed to the reduction of oxime group to amine. Typical cyclic voltammogram of 3,4-dichlorobenzophenone oxime in acetate buffer (pH 4.0) is given in Fig. 1. The

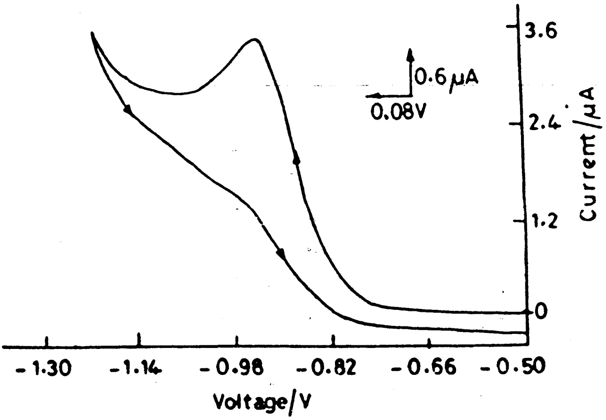


Fig. 1. Typical cyclic voltammogram of 3,4-dichlorobenzophenone oxime in acetate buffer of pH 4

Concentration = 0.5 mM

Solvent = 40% MeOH

Sweep rate = 40 mVs^{-1}

number of electrons involved in the electrode process was found to be four by millicoulometry[10]. Controlled potential reduction of 3, 4-dichlorobenzophenone oxime [pH 2.0, $E = -0.88$ V (SCE)] produced corresponding amine, which was confirmed by usual chemical tests.

The $E_{1/2}/E_p$ values are found to shift to more negative values with the increase in the pH of the medium indicating proton involvement in the electrode process. The nature of the waves and peaks was found to be diffusion controlled in the buffer systems taken, as shown by the linear dependance of limiting current on $h^{1/2}$ and constancy of the current function $i_p/Cv^{1/2}$ respectively.

The irreversibility of the electrode process was verified by logarithmic analysis of the wave. The slope of the E vs. log $i/i_d - i)$ plot exceeds appreciably $59.2/n$ mV and the numerical value of $E_{1/4} - E_{3/4}$ exceeds $54.6/n$ mV.[11]

An increase in the percentage of methanol in the polarographic test solution shifted the half-wave potentials towards a more negative potential with simultaneous decrease in diffusion current (Table 1). An increase in the organic solvent content resulted in a rise in pH[12, 13] and an increase in the dissociation constant of the protonated species.[14] Both of these factors lower the rate of protonation and consequently lead to shift in $E_{1/2}$ of the reduction towards more negative potentials.

TABLE 1

EFFECT OF INCREASING THE PERCENTAGE OF NON-AQUEOUS SOLVENTS ON $E_{1/2}$ OF 3, 4-DICHLOROBENZOPHENONE OXIME IN CLARKS AND LUBS BUFFER OF pH 2, C=0.5 mM

Methanol/%	$-E_{1/2}$/V	i_d/μA
40	0.82	4.94
50	0.83	4.52
60	0.85	4.13
70	0.87	3.97

The decrease in diffusion current may be partly due to an increase in the viscosity of the medium and partly to an ion-pair factor[15]. The ion-pair factor must be considered because a continuous decrease in the diffusion current was observed. It also appeared that the above factors are not the only ones responsible for the observed shift in $E_{1/2}$; for 3, 4-dichlorobenzophenone oxime the observed shift is greater than it should be owing to the change in pH and dissociation constant. This additional shift in $E_{1/2}$ may be ascribed to a decrease in adsorbability and hence surface concentration of the depolariser with increase in the percentage

TABLE 2

KINETIC PARAMETERS FOR THE REDUCTION PROCESS OF 3,4-DICHLOROBENZOPHENONE OXIME IN 40% METHANOL IN VARIOUS BUFFER SYSTEMS, C=0.5 mM

S. No.	Supporting electrolyte	D. C. Polarography				Cyclic Voltammetry			
		$-E_{1/2}/V$	$i_d/\mu A$	$D\times10^6$ cm. s^{-1}	$k^0_{f,h}$ cm. s^{-1}	$-E_p/V$	$i_p/\mu A$	$D\times10^6$ cm. s^{-2}	$k^o_{f,h}$ cm. s^{-1}
1	Clarks and Lubs buffer (pH 2)	0.82	4.94	0.91	1.40×10^{-9}	0.86	3.96	0.89	1.39×10^{-19}
2	Acetate buffer (pH 4)	0.89	4.73	0.85	6.97×10^{-11}	0.93	3.42	0.84	4.32×10^{-11}
3	Citrate buffer (pH 6)	0.96	4.53	0.83	1.79×10^{-12}	1.05	3.39	0.835	3.41×10^{-13}
4	Phosphate buffer (PH 8)	1.07	4.34	0.82	1.87×10^{-14}	1.16	3.13	0.79	1.98×10^{-15}
5	Carbonate buffer (pH 10)	1.16	3.07	0.64	4.85×10^{-17}	1.21	2.45	0.59	5.62×10^{-18}
6	Bates and Bower buffer (pH 12)	1.24	2.87	0.52	2.43×10^{-19}	1.29	2.13	0.43	3.42×10^{-20}

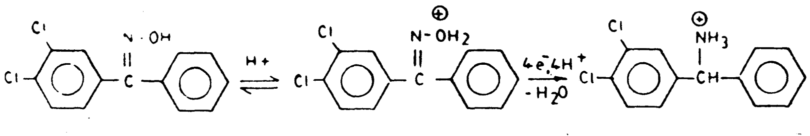
of non-aqueous solvent in the aqueous-organic mixture.[16] A decrease in surface concentration would retard the electrode process resulting in a decrease in $E_{1/2}$ and i_d.

The kinetic parameters for the electrode reaction have been obtained by using the methods given by Meites[17]. The values obtained for the diffusion coefficient (D) and heterogeneous forward rate constant ($k^o_{f,h}$) at various pH values are given in Table 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. D.C. polarographic diffusion coefficient values agree well with those calculated from cyclic voltammetric data. This is evident particularly since no adsorption is involved in electrode process. The heterogeneous forward rate constant values calculated are in general found to decrease with increase in the pH of the solution. This trend shows that the electrode reaction tends to become more and more irreversible with increase in pH[18]. The rate constant values are observed to be high in acidic medium indicating that the rate of reaction is fast in this medium when compared to basic medium, since in acid medium protonated form gets reduced.

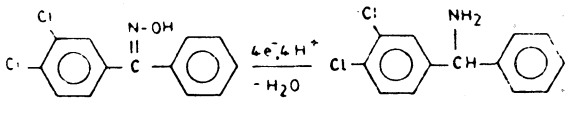
The following mechanism may be given for the reduction process at the mercury electrode in accordance with d.c. polarographic, cyclic voltammetric and controlled potential electrolysis data:

Reduction Mechanism

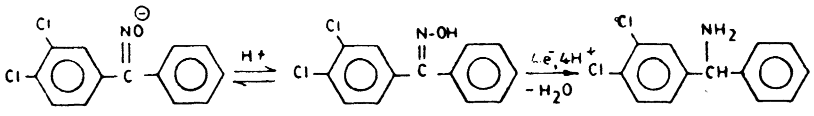
In acidic solutions, pH $\leqslant$ 2.



In neutral to alkaline solutions, pH $>$ 4 $<$ 8.



In the highly alkaline solutions, pH $>$ 10.



In the highly alkaline media pH $>$ 10, the anion of the oxime is the main species present which seems to get reduced in the present case.

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