Notes

Electrochemical studies on 4, 4'-dimethoxybenzophenone oxime

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The electrochemical reduction of 4, 4'-dimethoxybenzophenone oxime (4, 4'-DMBPO) has been studied at the mercury electrode in different supporting electrolytes, in the pH range 2.0-12.0 including 0.1 M $HClO_4$ in methanol-water mixture by employing cyclic voltammetry, d.c. polarography and millicoulometry. Kinetic parameters such as diffusion coefficient, transfer coefficient and forward rate constant values has been evaluated.

Ketoximes have important applications in medicine and analytical chemistry besides their importance in basic organic chemistry. In continuation of earlier work[1-6] from our laboratory on similar systems, we report here the results of electrochemical studies on 4, 4'-dimethoxybenzophenone oxime (4, 4'-DMBPO).

Experimental

4, 4'-DMBPO was prepared according to the literature method[1]. The purity of the compound was checked by its melting point. The supporting electrolytes employed in the present investigation were prepared in doubly distilled water from AR grade chemicals without further purification. A digital pH meter (model LI-120 Elico) was used for pH measurements. The solution of the title compound was prepared by dissolving a weighed amount in minimum amount of solvent and the volume was made up with the supporting electrolyte to obtain the desired concentration. Purified nitrogen gas was passed to maintain an inert atmosphere. Polarograms were recorded using a 364 Polarographic Analyser coupled with a Kipp and Zonen X/t recorder. A Metrohm E506 connected through VA-Scanner E612 coupled with digital electronics 2000 x-y/t recorder was used for recording the cyclic voltammograms. The DME used had the following characteristics: $m =$ 2.4132 mg/sec in buffer of pH 2.0 at a drop time of 3 sec. The area of HMDE used was 0.02626 cm².

Results and discussion

4, 4'-Dimethoxybenzophenone oxime was found to be reduced in two steps in all the supporting electrolytes employed in both the techniques. Typical cyclic voltammogram for 4, 4'-DMBPO in Clarks and Lubs buffer of pH 2.0 is presented in Fig. 1. In acidic and alkaline media, each step/wave is attributed to the reduction of oxime to imine with the addition of two electrons and imine to amine. The double-step polarogram shows the possibility of somewhat stable imine intermediate with a different reduction potential for the oxime. The number of electrons involved in the electrode process has been found to be four—two for the reduction of oxime to imine intermediate and two for imine to amine. This is further supported by the millicoulometric analysis (Table 1). The reduction process is found to be

Table 1—Typical millicoulometric data for 4, 4'-dimethoxy-benzophenone oxime

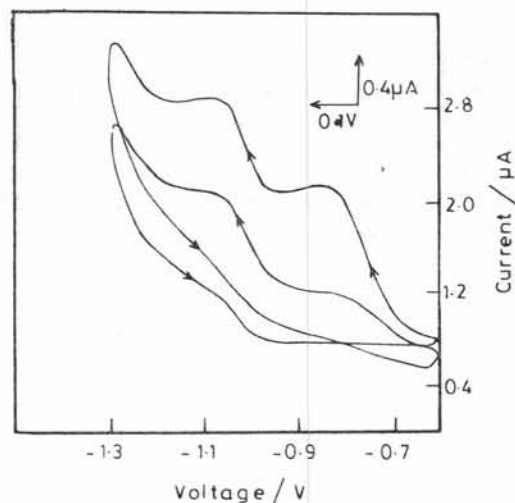|	Cell A (Cd²⁺)	Cell B	'n'
Diffusion current before electrolysis	i_1 (µA) 6.05	10.4	4
Diffusion current after electrolysis	i_2 (µA) 2.95	2.5	
Drop time before electrolysis t_1 (sec)	3.0	3.3	
Drop time after electrolysis t_2 (sec)	3.6	3.9	

Fig. 1—Typical cyclic voltammogram of 4, 4'-dimethoxybenzo-phenone oxime in Clarks and Lubs buffer: pH 2.0; sweep rate = 80 mVs⁻¹; conc. = 0.5 mM

Table 2—Typical kinetic parameters of 4, 4'-dimethoxybenzophenone oxime {conc.: 0.5 mM; drop time: 3 sec; sweep rate: 60 mVs⁻¹; solvent: 25% DMF}

Supporting electrolyte		Cyclic voltammetry			D.C. polarography		
		$-E_p$/V	$D \times 10^6/$ cm² s⁻¹	$k_{f,h}^0$/cm s⁻¹	$-E_{1/2}$/V	$D \times 10^6/$ cm² s⁻¹	$k_{f,h}^0$/cm s⁻¹
0.1 M HClO₄	(a)	0.63	6.04	4.3×10^{-11}	0.60	6.77	1.60×10^{-11}
	(b)	0.84	9.20	1.4×10^{-12}	0.82	9.05	7.20×10^{-22}
Clarks and Lubs buffer (pH 2.0)	(a)	0.82	8.30	3.36×10^{-12}	0.80	8.30	4.9×10^{-11}
	(b)	0.98	13.00	1.60×10^{-12}	0.98	8.30	7.2×10^{-22}
Acetate buffer (pH 4.0)	(a)	1.00			0.91		
	(b)	1.17	9.20	8.12×10^{-16}	1.19	10.2	4.2×10^{-16}
Phosphate buffer (pH 6.5)		1.15	17.0	2.7×10^{-16}	1.13	15.5	5.1×10^{-14}
McIlvaine buffer (pH 8.0)	(a)	1.48			1.48	5.38	
	(b)	1.69	13.0	2.98×10^{-22}	1.66	7.84	1.5×10^{-16}
Carbonate buffer (pH 10.0)		1.50	ill-defined		1.49	3.71	
					1.72	6.10	4.3×10^{-25}
Bates and Bower buffer (pH 12.0)		1.76	merging with hydrogen evolution		1.51	merging with hydrogen evolution	

(a) First wave; (b) second wave

irreversible as evidenced from the dependence of $E_p/E_{1/2}$ on concentration of electroactive species as well as compliance with Tomes' criterion. The irreversibility has also been confirmed by the absence of anodic peak in reverse direction in cyclic voltammetry and the slopes of log plot at various pH values. The polarograms in the alkaline region were not well formed and were seen to be affected by absorption as evident from the plots of diffusion current versus (height of mercury column)$^{1/2}$ and peak current versus (scan rate)$^{1/2}$ which are found to be not passing through the origin.

As the formation of the final reduction product consumes four electrons, the two polarographic steps are observed in the acidic and alkaline medium which correspond to two—electron additions on the basis of their wave heights. As the hydroxylamine derivative is not reducible at the potential encountered in the reduction of this oxime, the imine is taken as the possible intermediate[3,4]. The controlled potential electrolysis has indicated the final product to be amine with imine as the intermediate which has been isolated and confirmed by IR spectral studies of the electrolytic reduction products obtained through controlled potential electrolysis at -0.75 V versus SCE and -1.0 V versus SCE respectively. For imino group ($>CH=NH$), N−H and $>C=N$-stretching vibrations are observed at 3150 and 1640 cm⁻¹ respectively, whereas for amino group ($>CH-NH_2$), N−H stretching vibrations and N−H bending vibrations are observed at 3400 and 1600 cm⁻¹ respectively. The

$E_{1/2}$ and E_p of the first and second waves in the acidic medium showed a regular increase in the negative direction with pH, while in the alkaline medium the half-wave potential showed marginal increase. This might be taken as an evidence for the protonated oxime being the electroactive species in the acidic medium and the unprotonated molecule taking its place in alkaline medium. In highly alkaline media (pH > 10), the anion of the oxime is the main species present which seems reducible in the present case. The anion formed is shown to be electroactive probably due to the presence of methoxy groups on both sides of the oxime group. Based on the above results, the following mechanism may be postulated.

The kinetic parameters evaluated from both the techniques are presented in Table 2. There is a good agreement between diffusion coefficients obtained by d.c. polarographic and cyclic voltammetric methods in acidic media. Adsorption complicates the electrode process in alkaline media. When the percentage of the solvent increases, the diffusion coefficient values gradually decrease which may be attributed to the strong adsorption on the electrode surface by the solvent molecules. Diffusion co-efficients obtained by d.c. polarographic technique may be considered to be more reliable compared to the values obtained from other techniques in view of the advantages associated with the renewable nature of the dropping mercury electrode.

The heterogeneous forward rate constant values are in general found to decrease with increase in pH

ACIDIC MEDIA
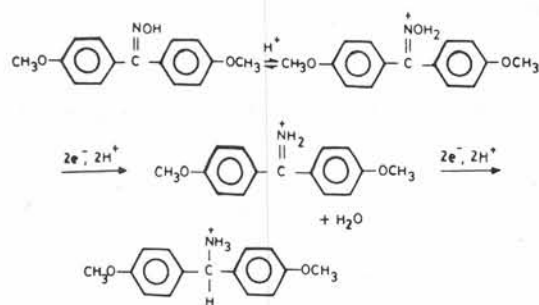
ALKALINE MEDIA
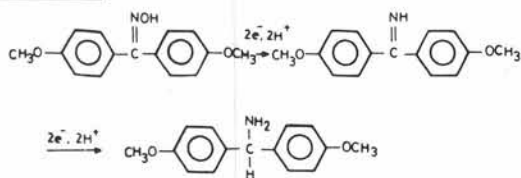
HIGHLY ALKALINE MEDIA
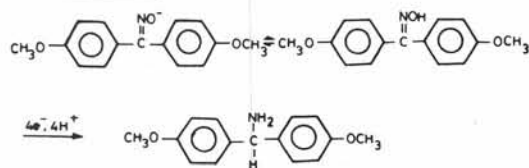
indicating that the electrode reaction tends to become more and more irreversible. The rate constant values are found to be high in acidic medium compared to those in alkaline medium indicating that the reaction is fast in acidic medium since the protonated form gets reduced. The forward rate constant values for the second wave are low, which might be due to the fact that the intermediate has a more negative reduction potential than the oxime which is evident from the better separation of two steps.

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