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Electrochemical Studies of Pralidoxime Chloride

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The electrochemical reduction behaviour of pralidoxime chloride (2-pyridinealdoxime methochloride) has been studied at a dropping mercury electrode (DMF) and hanging mercury drop electrode (HMDE) in various supporting electrolytes by making use of d.c. polarography, cyclic voltammetry, a.c. polarography, differential pulse polarography, millicoulometry and controlled potential electrolysis. The kinetic parameters such as diffusion coefficient and heterogeneous forward rate constant are evaluated and reported.

INTRODUCTION

D.C. polarographic technique is found to be extensively employed by previous investigation[1-7] to study the reduction behaviour of certain aldoximes and ketoximes. It has been shown that oximes undergo four-electron reduction giving rise to the corresponding amine. No attempt has been made to study the electrochemical behaviour of oximes by using advanced electrochemical techniques such as cyclic voltammetry, differential pulse polarography and a.c. polarography to the best of our knowledge. In addition the title compound is found to possess the ability to reactivate phosphorylated cholinesterase by nucleophilic attack and thus function as potential nerve gas antidote[8-10]. In view of the above facts, it is of interest to study the polarography of the title compound in order to understand the mechanistic aspects of the electrode processes involved and to evaluate these methods as analytical techniques for the determination of this compound. In the present investigation the reduction behaviour of the title compound has been studied in different aqueous supporting electrolytes such as Clarks & Lubs buffer (pH 2.0), acetate buffer (pH 4.0), McIlvaine buffer (pH 6.0), phosphate buffer (pH 8.0), carbonate buffer (pH 10.00) and Bates & Bower buffer (pH 12.0) and the reduction mechanism is proposed for the reduction of oxime group as well as 2-aminomethyl pyridinium system.

EXPERIMENTAL

2-Pyridinealdoxime methochloride has been prepared by resulting a solution of 2-pyridinealdoxime methoiodide (supplied from Sumitomo Chemical Co., Ltd., Japan) with silver chloride[10] and the resulting product was purified and used for preparation of solution of required concentration. The supporting electrolytes used were prepared in double distilled water from analaR grade chemicals. The solutions were deaerated with purified nitrogen gas. D.C. polarograms were recorded with Model 364 polarographic Analyzer (PARC) coupled with Kipp and zonen x/t recorder. Metrohm E 506 polarecored connected through Metrohm E 612 VA-Scanner and Digital Electronics 2000 x-y recorder was used for recording cyclic voltammograms. a.c. polarograms and differential pulse polarograms. The hanging mercury drop electrode used as working electrode in cyclic voltammetry had an area of 0.05548 cm^2. A dropping mercury electrode used in differential pulse polarography had an area of 0.02223 cm^2 at 2.0 seconds.

RESULTS AND DISCUSSION

2-Pyridinealdoxime methochloride is found to be reduced in two steps in all the buffers used and in all the techniques employed in the present investigation except in pH 2.0 in which the second peak is merged with the hydrogen evolution. The first peak is attributed to the reduction of oxime group corresponding to four-electron addition and the second peak due to the reduction of 2-aminomethylpyridinium chloride. A typical diffential pulse polarogram in pH 6.0 is shown in figure 1. The diffusion current/peak current is observed to be almost constant in the entire pH range studied and at the same time the half-wave/peak potential is noticed to be shifted to more negative values with increasing pH indicating the involvement of protons in the electrode process[11]. A distorted peak has been observed in alkaline media under DPP and a.c. polarographic conditions which may be attributed to the tautomerism[2, 5] of the electro-active species since oximes can show tautomerism as well as cis-trans

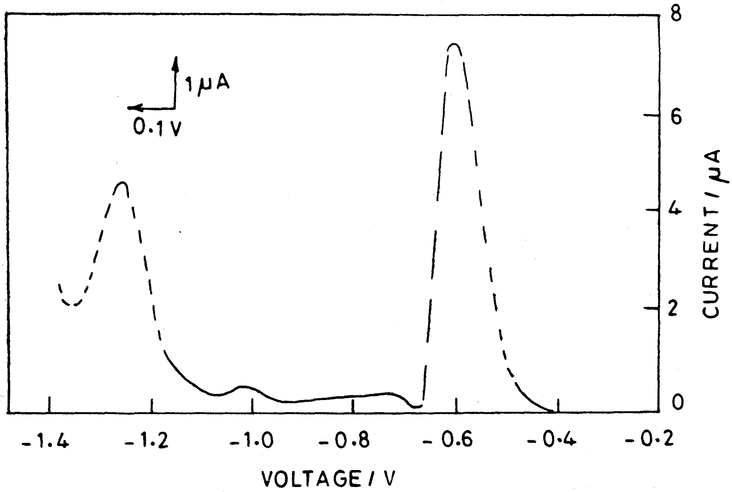


Fig. 1 Typical differential pulse polarogram of 2-pyridinealdoxime methochloride in the buffer of pH 6.0: Concentration = 0.489 mM, Drop time = 2.0 sec.

isomerism. The electrode process is found to be diffusion controlled as seen from the linear plots of i_d vs. c passing through origin indicating the absence of adsorption complications. But the adsorption complications are noticed in other techniques (Fig. 2) where depression of base current is observed before and after the a.c. peak. The reduction process is found to be irreversible as evidenced from the dependence of half-wave/peak potential on the concentration of the depolanizer and the deviation of a.c. polarographic summit potential from the d.c. polarographic half-wave potential. The irreversibility has been confirmed in cyclic voltammetry from the absence of anodic peak in the reverse direction.

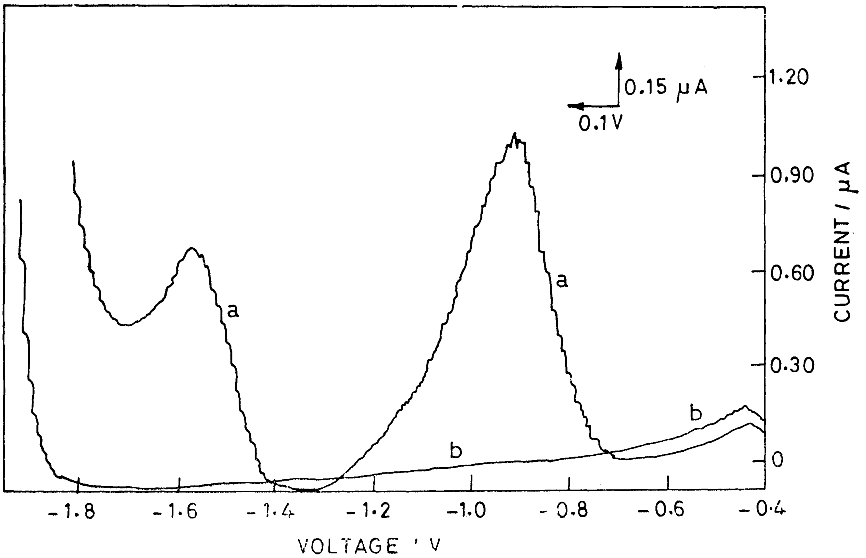


Fig. 2 Typical a.c. polarogram of 2-pyridinealdoxime methochloride in carbonate buffer of pH 10.0: Concentration = 0.489 mM, Drop time = 3.0 sec, a=a.c. peak, b=base line.

The number of electrons involved in the electrode process has been confirmed to be four for the first step and two for the second step with millicoulometric technique. The product was identified as amine by performing the controlled potential electrolysis at the first plateau and the final product may be 2-methyl-N-methylpyridinium chloride. The kinetic parameters such as diffusion coefficient and heterogeneous forward rate constant are evaluated and reported in Table 1.

The diffusion coefficient is observed to be followed the same order in all the techniques employed in the present investigations. But the d.c. polarographic diffusion coefficients may be taken as more reliable when compared to other techniques due to the absence of adsorption complications. The hetrogeneous forward rate constant values are found to be almost constant in each technique. The cyclic voltammetric rate constants

TABLE 1

TYPICAL KINETIC DATA OF PRALIDOXIME CHLORIDE (OXIME REDUCTION) CONCENTRATION = 0.489 mM

S.No.	Supporting electrolyte	Cyclic voltammetry		Differential pulse polarography		D. C. Polarography	
		$D \times 10^6/cm^2 s^{-1}$	$k^0_{f,h}/cm\ s^{-1}$	$D \times 10^6/cm^2 s^{-1}$	$k^0_{f,h}/cm\ s^{-1}$	$D \times 10^6/cm^2 s^{-1}$	$k^0_{f,h}/cm\ s^{-1}$
1.	Clark & Lubs buffer (pH 2.0)	2.528	2.571×10^{-12}	4.857	7.091×10^{-11}	7.705	2.161×10^{-5}
2.	Acetate buffer (pH 4.0)	2.285	1.577×10^{-12}	4.961	5.825×10^{-19}	7.705	7.253×10^{-8}
3.	McIlvaine buffer (pH 6.0)	2.503	6.474×10^{-14}	2.580	5.718×10^{-18}	8.072	4.101×10^{-9}
4.	Phosphate buffer (pH 8.0)	2.602	9.145×10^{-14}	3.160	1.853×10^{-14}	8.072	1.703×10^{-8}
5.	Carbonate buffer (pH 10.0)	2.996	1.055×10^{-13}	2.791	3.069×10^{-16}	8.072	2.078×10^{-9}
6.	Bates & Bower buffer (pH 12.0)	2.464	1.559×10^{-20}	distorted peak		8.448	2.944×10^{-8}

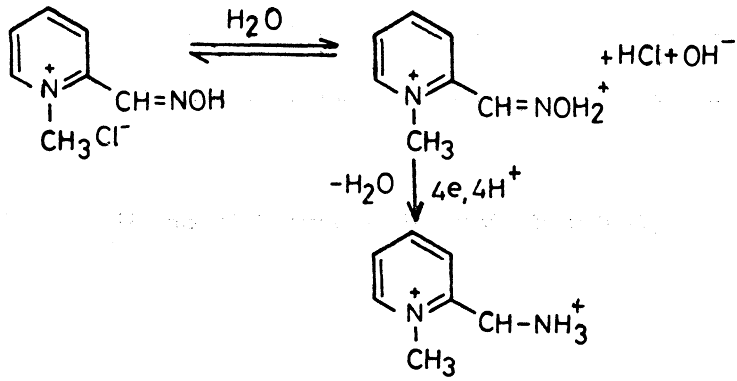
are noticed to be relatively low when compared to d.c. polarographic values since the latter technique is a non-steady state one. Differential pulse polarographic rate constants are still lower due to the different nature of this technique from the former two.

D.C. polarography and differential pulse polarography have been used for the qualitative estimation of 2-pyridinealdoxime methochloride with calibration as well as standard addition methods. D.C. polarography is found to be the appropriate technique for analysis of the title compound present at higher concentration in the given unknown solution in all the supporting electrolytes in view of the absence of adsorption complications *in this* technique. For analysis of 2-pyridinealdoxime methochloride at lower concentrations, the differential pulse polarographic technique is found to be more suitable due to its high sensitivity.

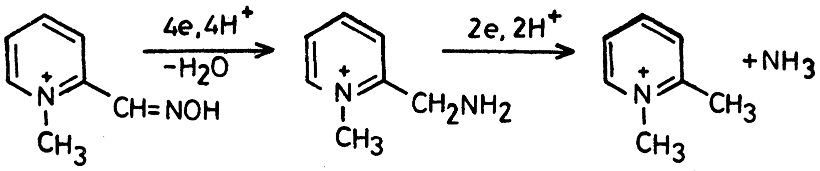
REDUCTION MECHANISM

The results of the product analysis are observed to be in good agreement with the fact that the product of the oxime group reduction is the corresponding amine and the amine getting reduced in the two electron step which is also supported by Gomez Nieto *et al*[12, 13]. Hence, the reduction pathway can be represented as:

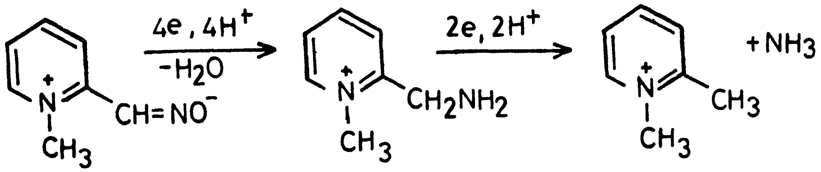
(i) In acidic solutions, pH = 2



(ii) In neutral to alkaline solutions, pH = 4



(iii) In alkaline solutions, pH = 10



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