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Electrochemical Behaviour of Pentachloronitrobenzene

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Electrochemical behaviour of pentachloronitrobenzene PCNB has been studied at dropping mercury electrode and hanging mercury drop electrode in differing supporting electrolytes covering a pH range from 2.0 to 12.0 in DMF-water mixtures by making use of the techniques d.c. polarography, cyclic voltammetry, a.c. polarography, millicoulometry and controlled potential electrolysis. The kinetic parameters are evaluated and reported. The nature of the reduction process of the electroactive species is discussed.

INTRODUCTION

Smyth and Osteryoung[1] have examined the pulse polarographic behaviour of pentachloronitrobenzene (PCNB). They have found that differential pulse polarography can be used to differentiate between parathion, *p*-nitrophenol and pentachloronitrobenzene. But a systematic study was not made in aqueous media and details regarding the electrode kinetics were not given. Due to its important role in agricultural field for pest control, it is of interest to understand the reaction mechanism and electrode kinetics by employing electrochemical techniques and to develop a method for analysis of the compound present at low concentrations.

EXPERIMENTAL

The compound PCNB was supplied by Promochem, (West Germany). The purity of the compound was tested by melting point determination. Stock solution was prepared by dissolving the required amount of PCNB in dimethylformamide as a solvent and making up with the supporting electrolytes to get the desired concentration. All the supporting elecrolytes used in this work were of analytical grade.

RESULTS AND DISCUSSION

The electrochemical behaviour of PCNB is examined in different supporting electrolytes covering a pH range from 2.0 to 12.0. Below pH 6.0, one single reduction wave/peak is well formed which displayed good reproducibility. The single wave/peak is attributed to the reduction of nitro group to hydroxylamine with four-electron addition. Above pH 6.0, this wave/peak is found to split into two wave/peaks of equal size. A typical cyclic voltammogram in Bates and Bower buffer of pH 12.0 is shown in Fig. 1.

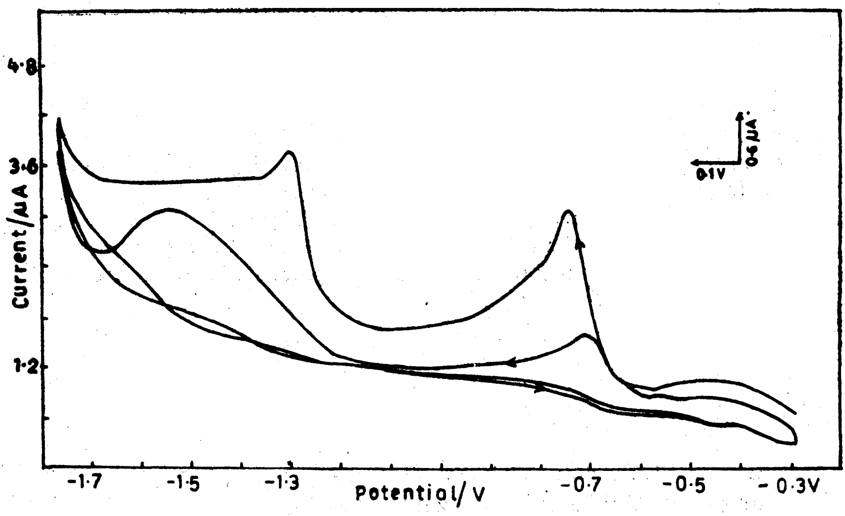


Fig. 1. Typical cyclic voltammogram of PCNB in Bates and Bower buffer (pH 12.0), Concentration: 0.38 mM, Sweep rate: 40 mVs^{-1}, Solvent: 40% DMF.

Generally, nitro groups[2] are reduced with the addition of six electrons to the corresponding amine in two step process, or with the participation of four electrons as for as the hydroxylamine. As seen from the results of above experiments, it is found to be only four electron addition in PCNB. Since the proximity between chlorine atoms and nitro group, and also the mesometric effect of chlorine group on benzene ring, the required positive charge is not developed on the nitro group. Because of the operation of these effects, the reduction is likely to be stopped at first stage only.

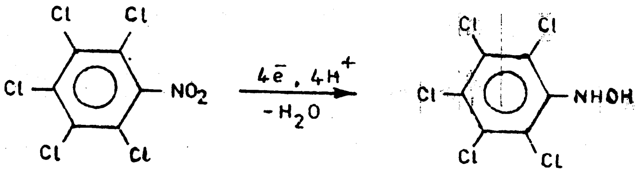
Conventional log-plot analysis, variation of $E_{1/2}$ and E_p values towards more negative potentials with increase of concentration of depolarisor, the deviation of a.c. polarographic half-wave potentials and absence of anodic peak in the reverse scan in cyclic voltammetry show that the electrode process related to the reduction of PCNB is irreversible. The diffusion controlled nature of the electrode process is evidenced from the linear plots of i_d vs. $h^{1/2}$, i_p vs. $V^{1/2}$ passing through origin in all the supporting electrolytes indicate the absence of adsorption complications in all the media studied.

Controlled potential electrolysis is carried out in Clarks and Lubs buffer of pH 2.0 and Bates and Bower buffer of pH 12.0 at −0.25V, −1.20V respectively. The product formed after controlled potential electrolysis is identified as hydroxylamine by spot test[3] in both the supporting electrolytes mentioned above. Millicoulometry is also employed in Clarks and Lubs buffer of pH 2.0 and Bower buffer of pH 12.0 to find out '*n*' values involved in the electrode process. The results show the number of electrons involved in the electrode process as four.

On the basis of the results obtained, the following reduction mechanism may be proposed for PCNB in different zones of pH.

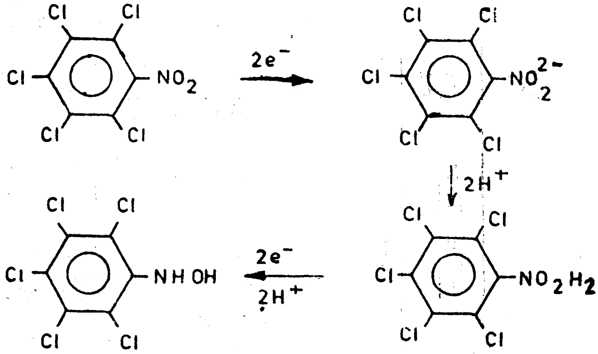
In acid medium: $2.0 < pH < 6.0$

In this medium, PCNB is reduced in single four electron step corresponding to the reduction of nitro group to the hydroxylamine.



In alkaline medium: $6.0 < pH < 12.0$

In this medium, a two step two-electron addition occurs allowing the reduction of nitro group to go up to the corresponding hydroxylamine. The first wave/peak corresponds to the two electron reduction of $-NO_2$ to $-NO_2^{2-}$. The second wave/peak is attributed to the reduction of $-NO_2^{2-}$ to −NHOH.



The kinetic parameters for the electrode process have been evaluated and reported in Table 1. The variation of diffusion current and peak current with the pH of the supporting electrolyte influences the diffusion

TABLE 1

TYPICAL ELECTRODE KINETIC DATA FOR PCNB

Conc: 0.38 mM Percentage of solvent: 40% DMF Sweep rate: 40 mVs⁻¹

Name of the supporting electrolyte	d.c. polarography			Cyclic voltammetry			a.c. polarography			Differential pulse polarogram Conc: 0.038 mM 10% DMF		
	$\frac{-E_{1/2}}{V}$	$\frac{D\times10^6}{cm^2\,s^{-1}}$	$\frac{k^o_{f,h}}{cms^{-1}}$	$\frac{-E_p}{V}$	$\frac{D\times10^6}{cm^2\,s^5}$	$\frac{k^o_{fh}}{cms^{-1}}$	$\frac{-E_s}{V}$	$\frac{D\times10^6}{cm^2\,s^{-1}}$	$\frac{k_f}{cm\,s^{-1}}$	$\frac{-E_m}{V}$	$\frac{D\times10^7}{cm^2\,s^{-1}}$	$\frac{k^o_{f,h}}{cms^{-1}}$
Clarks and Lubs buffer pH 2.0	0.15	1.79	1.78×10^{-2}	0.28	2.72	5.16×10^{-10}	0.35	0.66	1.12×10^{-4}	0.34	9.48	7.67×10^{-12}
Acetate buffer pH 4.0	0.33	1.58	3.91×10^{-5}	0.40	2.58	1.84×10^{-12}	0.42	0.56	1.03×10^{-4}	0.45	7.09	1.87×10^{-14}
Phosphate buffer (a)	0.53	2.27	1.99×10^{-9}									
pH 6.0 (b)	1.21	2.81	6.14×10^{-10}	0.56	0.16	2.62×10^{-16}	0.64	0.44	9.16×10^{-5}	0.56	4.32	2.56×10^{-17}
McIlvaine buffer (a)	0.57	2.81	1.98×10^{-10}	0.64	0.58	1.19×10^{-17}						
pH 8.0 (b)	1.25	2.53	9.70×10^{-12}	0.87	0.28	1.79×10^{-22}	0.73	0.39	5.08×10^{-5}	0.62	3.35	6.02×10^{-19}
Carbonate buffer (a)	0.64	3.09	3.28×10^{-12}	0.72	0.48	2.58×10^{-19}	0.94	0.56	1.03×10^{-4}	0.69	4.37	4.03×10^{-20}
pH 10.0 (b)	1.28	2.27	4.76×10^{-13}	0.93	0.12	7.08×10^{-24}	1.12	0.81	1.20×10^{-4}	0.85	2.35	2.66×10^{-19}
Bates and Bower (a)	0.66	4.04	6.16×10^{-13}	0.74	0.12	1.48×10^{-19}	0.96	0.82	1.21×10^{-4}	0.86	2.79	3.32×10^{-23}
buffer pH 12.0 (b)	1.28	2.27	4.38×10^{-13}	1.30	0.79	1.21×10^{-89}	1.32	0.50	9.69×10^{-4}	1.08	3.80	2.18×10^{-24}

(a) First wave/peak.

(b) Second wave/peak.

coefficient values also to vary in the same manner. The reason for slight variations in diffusion coefficient values with increase in pH may be attributed to the non-availability of protons with increase in pH. Differential pulse polarographic diffusion coefficient values are in general found to be less, probably due to the lower concentrations taken in this sensitive technique. The rate constant values are found to decrease with increase in pH as expected. This trend shows that the electrode reaction tends to become more irreversible with increasing pH of the solution. The rate constant values are observed to be high in acidic medium indicating the rate of reaction to be fast in acidic media since the protonated form is getting reduced.

With the increase in the solvent composition, the wave/peak potentials are found to increase towards more negative potentials which may be explained as due to the possible adsorption of the solvent molecules on the surface of the electrode making the reduction difficult[4].

ANALYSIS

In the present investigation, d.c. polarography and differential pulse polarography have been used for the quantitative estimation of PCNB. The calibration plots are obtained by plotting current values against concentrations of the electroactive species. The calibration plots thus obtained are used for estimating the concentration of unknown samples. The lower detection limit is noticed to be 0.4×10^{-5} m and 4.0×10^{-7} M in d.c. polarography and differential pulse polarography respectively. For analysis of PCNB, the differential pulse polarographic technique is found to be more suitable due to its high sensitivity and resolution. Standard addition method is used for the estimation of PCNB, in the unknown samples. *Recommended procedure* (DPP): The solution is prepared by dissolving the required quantity of PCNB in the solvent, DMF and made up with the supporting electrolyte to get the 1.0×10^{-5} M concentration of standard solution. Supporting electrolyte of 2.0 pH 6.0 in 10% DMF is found to be the suitable medium for the determination of PCNB. 1 ml of the standard solution is transferred to a polarographic cell and made up with 9 ml of the supporting electrolyte to get the concentration of 1.0×10^{-6} M and then deoxygenated with nitrogen. After recording blank polarogram, small increments are added (i.e., 1 ml of standard solution) and polarograms taken after each addition. Concentration of unknown sample solution is calculated. In the present work, a modulation amplitude of 60 mV and drop time of 2 sec. are chosen as being suitable for analytical purposes. The relative standard deviation of this method is found to be 1.84% (10 replicants). The correlation of coefficient is seen to be 0.221 in this method.

REFERENCES

1. M. R. Smyth and J. C. Osteryoung, *Anal. Chem. Acta.*, **96**, 335 (1978).
2. J. C. Lawless, D. E. Bertek and M. D. Hawelyi, *J, Amer Chem. Soc.*, **91**, 1721 (1969).
3. F. Feigel, Spot tests in Organic Chemistry, Elsvier publishing house, Amsterdam, Chapter 3, 284.
4. K. Ganapathi and M. Ramanujam, *Indian J. Chem.*, **21A**, 8 (1982).

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