MJS, Vol.1, No.1, May-Oct. 2002, pp15 - 27
ISSN 0975-3311
https://doi.org/10.12725/mjs.1.2 | 15-27

A STUDY ON THE POLAROGRAPHIC BEHAVIOUR OF CYCLOPENTANONE OXIME

Charmaine Jerome *

Abstract

A study on the polarographic behaviour of cyclopentanone oxime has been carried out to analyse the nature of the reduction process, to calculate the number of electrons and protons involved in the process, to find out how the half-wave potentials vary with concentration and pH, and to present a possible mechanism for the reduction process.

Introduction

The electrolysis[1] of organic compounds has been carried out for almost a century, but for a long time, there was a rather limited understanding of the processes involved. Polarography has contributed more to the understanding of processes involved in the electrolysis of organic substances than any other method.

Polarography[2] is an electrochemical technique which makes use of current - voltage curves under conditions of concentration polarization of an indicator electrode. The method was first described by J.Heyrovsky in 1922. The technique involves recording the current at the dropping mercury electrode (DME) as the applied voltage is gradually increased.

The study of polarographic electrolysis contributed considerably to our understanding of transport phenomena, of the role of potential control in electrolysis and of effects of chemical reactions antecedent, parallel or consecutive to the electrode process proper.

* Senior Lecturer, Dept. of Chemistry, Mount Carmel College, Bangalore - 560 052

After the theoretical relationships between the limiting current and concentration had been derived by D. Ilkovic, polarography found wide application as an analytical method. The sensitivity, the small volume of sample and in particular the sensitivity of polarographic methods were the main factors contributing to its growth and importance.

In organic chemistry[3], polarography can be used in the determination of equilibrium rate constants, in studies of reaction mechanisms, in the search for optimal conditions for some preparative reactions, in studies and comparisons of reactivities of organic compounds and in correlations of structure with polarographic data.

Polarographic curves, identifications of electrolysis products and intermediates, structural effects and combination with other methods may be used for the elucidation of organic electrode process at the DME.

During recent years, the polarographic behaviour of a large number of organic compounds has been investigated.

Preparation of Cyclopentanone Oxime

10 g of hydroxylamine hydrochloride and 16 g of crystallised sodium acetate were dissolved in water in a 100 ml conical flask. The solution was warmed to about 40°C and 10 ml of cyclopentanone was added. The flask was closed with a cork and was shaken vigorously for a few minutes. The oxime was soon separated. The flask was cooled in ice and the crystals were filtered. It was recrystallised from petroleum ether. The yield was reported to be 7 g. The melting point was determined and it was in agreement with the theoretical value. (M. Pt. 56.5°C). It was further confirmed by its I.R. Spectra. Characteristic peaks were obtained at $3200cm^{-1}$ and $1690cm^{-1}$.

Sample Preparation

The sample to be analysed polarographically was taken in a suitable solution having a reasonable dielectric constant that can neither be reduced nor oxidised at the mercury electrode. This solution was the supporting electrolyte. In the present study, O.1N KC1 was used as the supporting electrolyte. Its decomposition potential being very negative, its reduction current wave was well beyond the range of the test sample studied. It did not react with the electro active substance (cyclopentanone oxime) in the solution nor with the metallic mercury. Its concentration being 100 times greater than the test solution, ensures the complete elimination of migration currents.

The reaction mixture was prepared in such a way that the concentration of cyclopentanone oxime was $1 \times 10^{-3}M$; concentration of KC1 was

0.1 M; Britton Robinson buffer solution was of pH = 3.4. The solvent used was water. By operating the potential scanning unit and recorder of the Polarograph, the corresponding polarographic wave was recorded.

By varying the concentration of cyclopentanone oxime (0.001 M, 0.0004 M, 0.0006 M, 0.0008 M) and keeping other factors like pH, and temperature as constant, the experiment was carried out to study the effect of concentration variation (Table - 1).

CONCENTRATION VARIATION OF CYCLOPENTANONE OXIME

Table - 1

Concentration	I_d in μA	$E_{½}$ in volts
0.0004 M	12.6	-1.05
0.0006 M	16.8	-1.10
0.0008 M	28.8	-1.04
0.001 M	30.6	-1.04

Polarographic runs were also obtained by varying the pH of the medium from 3 to 10 using Britton - Robinson buffer (Table - 2) and maintaining other factors constant for the cyclopentanone oxime.

pH VARIATION OF CYCLOPENTANONE OXIME

Table - 2

pH	I_d in μA	$E_{½}$ in volts
3.3	27	-1.07
3.67	10.8	-1.03
4.21	7.2	-1.03

CONCENTRATION VARIATION OF CYCLOPENTANONE OXIME

Table - 3

Conc. of cyclopentanone oxime = .0004 M ; Height = 41.5 cm

Conc. of KC1 = 0.1 M ; pH = 3.4

Solvent = Water ; Temp. = 307° K

-E V	Log $\frac{i}{i_d - i}$	-E V	Log $\frac{i}{i_d - i}$
1.2	-1.3010	1.3	0.0414
1.22	-0.9777	1.32	0.3010
1.24	-0.7782	1.34	0.7782
1.26	-0.5051	1.36	0.9777

I_d = 12.6 μA E½ = -1.05 V

Table - 4

Conc. of cyclopentanone oxime = .0006 M ; Height = 41.5 cm

Conc. of KC1 = 0.1 M ; pH = 3.4

Solvent = Water ; Temp. = 307° K

-E V	Log $\frac{i}{i_d - i}$	-E V	Log $\frac{i}{i_d - i}$
1.14	-1.4314	1.26	-0.3979
1.18	-1.1139	1.28	-0.0621
1.2	-0.9208	1.30	0.3245
1.22	-0.7782	1.32	0.9208
1.24	-0.6628	1.34	1.4314

I_d = 16.8 μA E½ = -1.10 V

pH VARIATION OF CYCLOPENTANONE OXIME

Table - 5

Conc. of cyclopentanone oxime = .001 M ; Height = 41.5 cm

Conc. of KC1 = 0.1 M ; pH = 3.30

Solvent = Water ; Temp. = 308° K

-E V	Log $\frac{i}{i_d - i}$	-E V	Log $\frac{i}{i_d - i}$
1.12	-1.6435	1.26	-0.5980
1.16	-1.3324	1.28	-0.3010
1.18	-1.1461	1.3	-0.0969
1.2	-1.0107	1.32	-0.3912
1.22	-0.9031	1.34	-0.8129
1.24	-0.8129	1.36	1.3324

I_d = 27 μA E½ = -1.07 V

pH VARIATION OF CYCLOPENTANONE OXIME

Table - 6

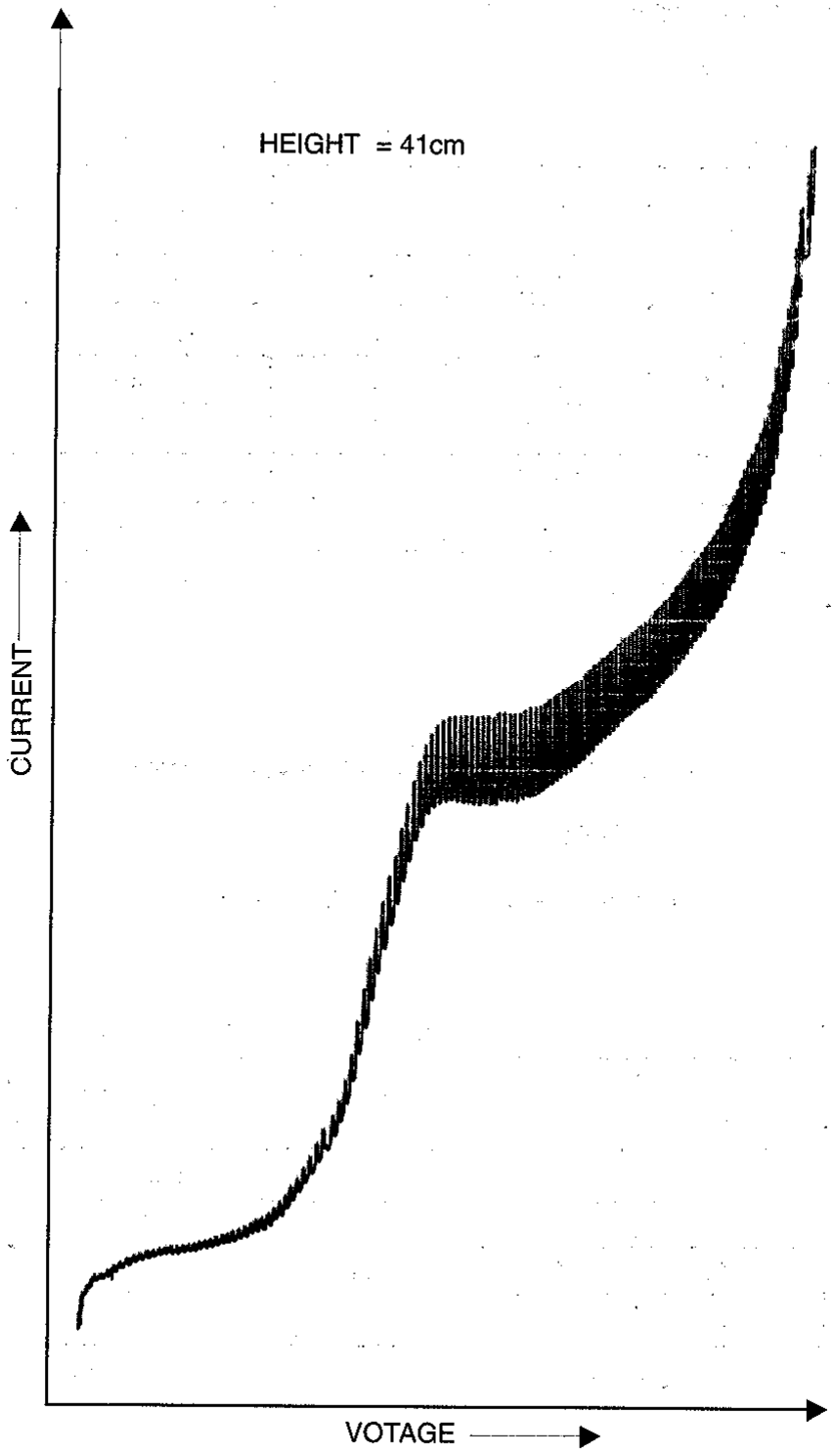
Conc. of cyclopentanone oxime = .001 M ; Height = 41.5 cm

Conc. of KC1 = 0.1 M ; pH = 3.67

Solvent = Water ; Temp. = 308° K

-E V	Log $\frac{i}{i_d - i}$	-E V	Log $\frac{i}{i_d - i}$
1.18	-1.2304	1.28	0.0969
1.2	-0.9031	1.3	0.4149
1.22	-0.6989	1.32	0.5441
1.24	-0.3010	1.34	1.2304

I_d = 10.8 μA $E_{½}$ = -1.03 V


HEIGHT = 41cm
CURRENT
VOTAGE

Results and Discussion

The polarograms of the various solutions of cyclopentanone oxime were obtained with automotive D.C. recording polarograph. The potentials were measured against a saturated calomel electrode. The dropping mercury electrode had the following characteristics at a mercury height of 41 cm.

$$m^{2/3} = 1.7203 \text{ mg/sec.} \; ; \; t^{1/6} = 1.3480 \text{ sec.}$$

Cyclopentanone oxime gets reduced at the dropping mercury electrode giving a well defined single wave in the pH range of 3.1 to 4.2.

The half wave potential E½, was calculated by plotting E vs log $\frac{i}{i_d - i}$

Polarograms were recorded at different concentrations of the cyclopentanone oxime. The diffusion current Id was found to vary linearly which concentration.

In order to calculate the number of electrons involved in the electro-reduction of cyclopentanone oxime, the Ilkovic equation.

$$n = \frac{I_d}{{}_{607}\, C D^{1/2}\, {}_m{}^{2/3}\, {}_t{}^{1/6}}$$

was employed.

The diffusion coefficient 'D' was found out by making use of the Stock - Einstein equation,

$$D = \frac{3.32 \times 10^{-5}}{\eta\, (v_m)^{1/3}}$$

Where η is the viscosity and V_m is the molar volume. Using the calculated D value, 'n' was found to be equal to 4.16. Hence the number of electrons involved in the electrode process for the given compound is assumed to be four.

The kinetic parameter (transfer coefficient $\propto$ n) has been calculated using Meites and Israels extended method[4] at different pH.

The plots of E Vs log $\frac{i}{i_d - i}$ were linear and their slopes were equated

to $\frac{2.303\ RT}{\alpha_n F}$ from which α_n were calculated (Table - 7)

Table - 7

pH	Slope	α_n
3.3	0.126	0.434
3.67	0.066	0.92
4.21	0.077	0.786

Effect of pH

The polarographic reduction of cyclopentanone oxime is highly dependent on pH. This reaction was studied at different pH (2.4 to 7). A well defined polarographic wave was obtained in the pH range of 3.1 to 4.2. Throughout this pH range only one polarographic wave was obtained for this compound. Cyclopentanone oxime gets reduced in the acid medium. The reduction was not noticed in the alkaline medium.

The results indicate a smooth decrease in the height of the wave. (Table - 8).

Table - 8

pH	I_d μA	$E_{½}$ Volts
3.3	27	-1.07
3.67	10.8	-1.03
4.21	7.2	-1.03

Figure - 1

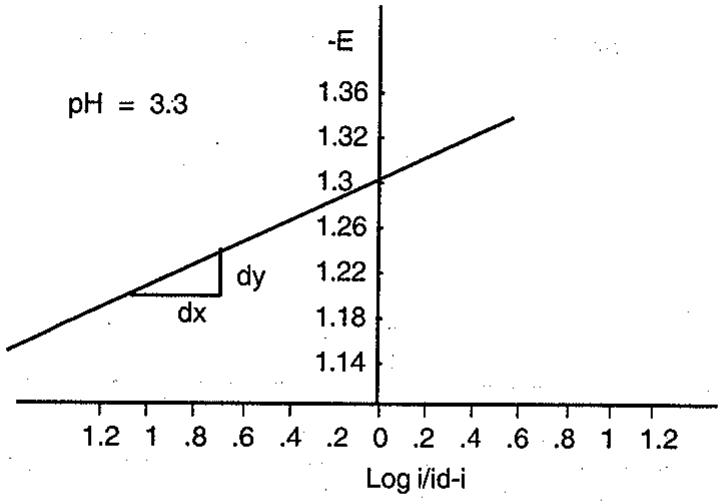


Figure - 2

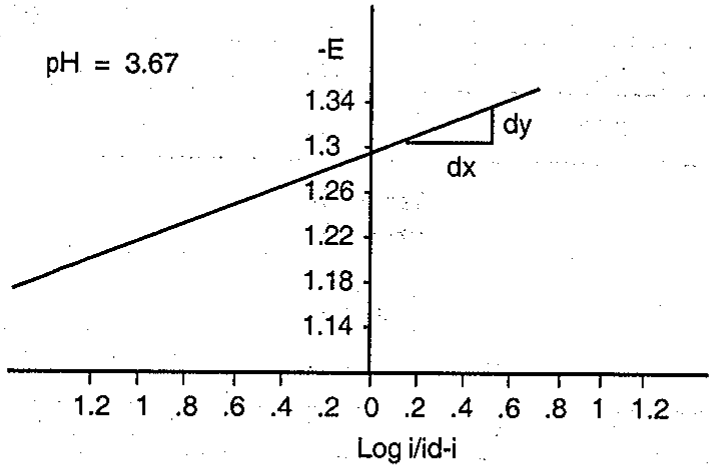
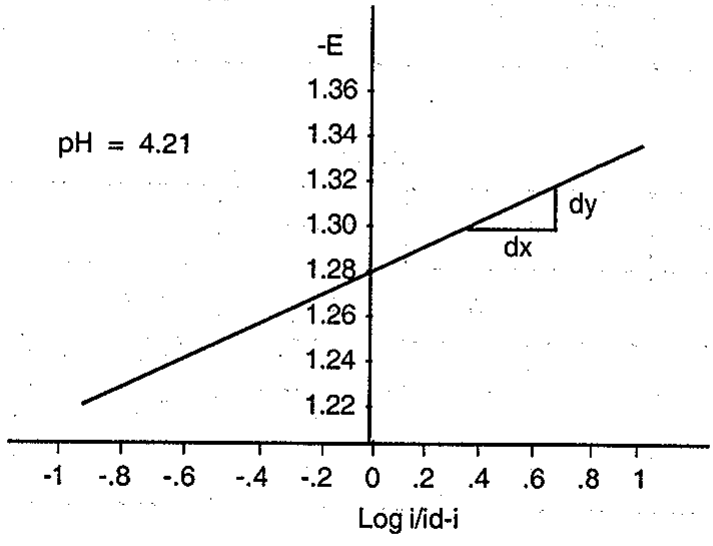


Figure - 3



Mechanism

Potential dependent rate constant was calculated using the following expression[5],

$$k = \left(\frac{7D}{3\pi t}\right)^{1/2} \left(\frac{i}{i_d - i}\right)$$

for different potentials.

Table - 9
pH = 3.3

E volts	K	Evolts	K
1.12	1.532×10^{-5}	1.22	8.43×10^{-5}
1.16	3.137×10^{-5}	1.24	1.037×10^{-4}
1.18	4.818×10^{-5}	1.26	1.702×10^{-4}
1.2	6.57×10^{-5}	1.28	3.37×10^{-4}

Table - 10
pH = 3.67

E volts	K	Evolts	K
1.18	3.96×10^{-5}	1.26	5.4×10^{-4}
1.2	8.43×10^{-5}	1.28	8.43×10^{-4}
1.22	1.35×10^{-4}	1.3	1.75×10^{-3}
1.24	3.37×10^{-4}	1.32	2.363×10^{-3}

Table - 11

pH = 4.21

E volts	K	Evolts	K
1.2	6.13×10^{-5}	1.28	6.75×10^{-4}
1.22	1.35×10^{-4}	1.3	1.35×10^{-3}
1.24	2.25×10^{-4}	1.32	3.37×10^{-3}
1.26	3.37×10^{-4}	1.34	7.43×10^{-3}

When log K was plotted against E_{dme} (Figure - 4, 5, 6) only one straight line was obtained in the pH range, showing that only one rate determining step exists in the reduction of cyclopentanone oxime.

Figure - 4

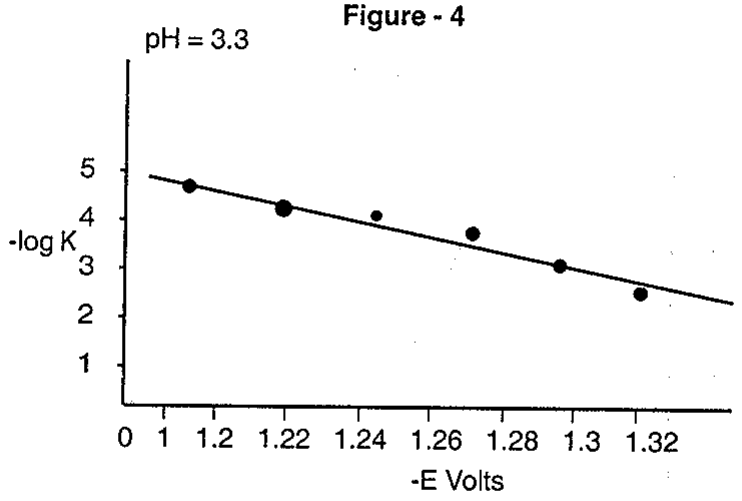


Figure - 5

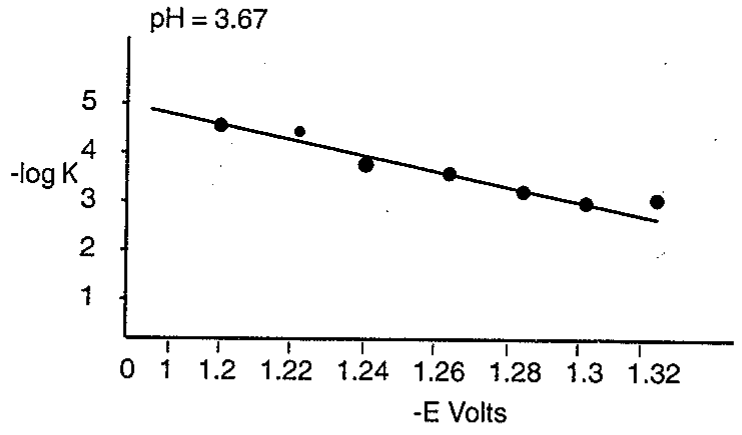
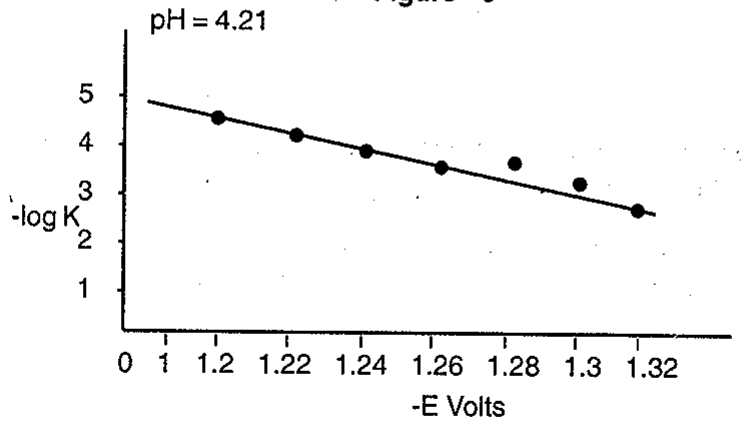
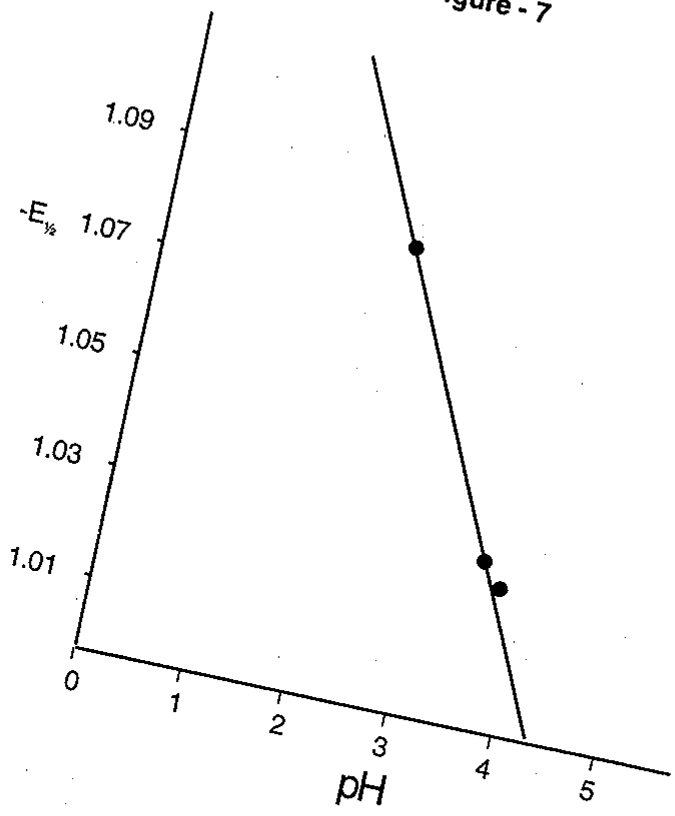


Figure - 6



The number of protons involved in the rate determining step of the reduction of the cyclopentanone oxime was calculated from the slope of the plot of $E_{½}$ Vs pH (Figure - 7).

Figure - 7

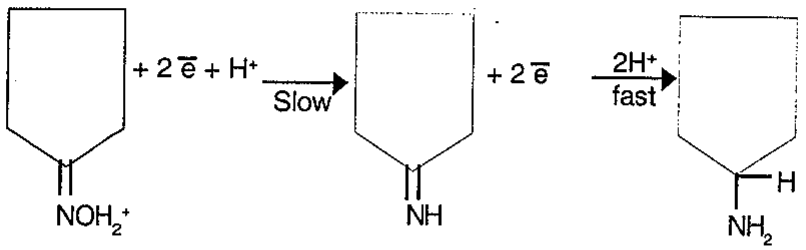


$$\text{Slope} = \frac{2.303\ RT}{\alpha_n F} \times P$$

It is observed to be 1.4, which indicates that protons involved in the rate determining step is 1.

On the basis of the foregoing observations, the probable mechanism for the 4 electron reduction of cyclopentanone oxime can be written as follows.

in acid medium



Summary

It has been found out that cyclopentanone oxime gets reduced at the dropping mercury electrode, giving a well defined single wave in the pH range of 3.1 to 4.2. The irreversible nature of the polarographic reduction of cyclopentanone oxime was also established. Various polarographic kinetic parameters are found out for the compound under study. The effect of pH, and concentration on the diffusion current and half wave potential has been established. Cyclopentanone oxime is found to undergo four electron reduction, and a probable mechanism for the reduction process is also suggested.

References

1. Zuman, P., 'Topics in Organic Polarography'. 25, 176 (1961).

2. Crow, D.R., 'Principles and Applications of Electrochemistry'.

3. Baizer Manuel, M., 'Organic Electrochemistry'.

4. Meites, L., and Israel, Y., J. Amer. Chem. Soc.83, 4903(1961).

5. Vijayalakshmamma, S.K., & Subramanya, R.S., Ind. J. Chem., 21 A, 1265 (1982).

6. Zuman, P., 'Topics in Organic Polarography'. 26, 176 (1961).