Electrochemical reduction of alloxan monohydrate on HMDE

Sheela Berchmans and R Vijayavalli

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

Alloxan monohydrate (AM) is a fully oxygenated pyrimidine and has been the subject of intensive study owing to its importance in biological systems. The hydrated carbonyl group in the 5th position is known to be active functional group. The electrochemical reduction of AM has been investigated by cyclic voltammetric technique using HMDE at pH 1.0 to 5.0 using acetate buffer. The range of potential scan employed was from +200 mV to -1.5V vs SCE and the scan rate was varied from 10 mV.s^{-1} to 640 mV.s^{-1} and the experiments were carried out in nitrogen atmosphere. Two reduction peaks PC_I and PC_{II} were observed around 40 mV -200 mV and around -850 mV to -900 mV vs SCE depending upon the pH. On the anodic side also two peaks were observed. All the peaks were dependent on pH and scan rate. At low pH, PC_I was a plateau while Pa_I was absent. The reduction reaction was found to occur in two stages, namely, dehydration of AM followed by its reduction to dialuric acid at low pH, whereas at high pH this two stage reduction and reduction of dehydrated alloxan compete with each other. The product formed was confirmed by U.V. & I.R.

Key words: Alloxan monohydrate, electroreduction, HMDE

INTRODUCTION

A lloxan monohydrate has been a subject of intensive investigation among biochemists because when administered to experimental animals it caused diabetes [1]. The electrochemical reduction has been studied with a view to understand the mechanism of reduction and to calculate the kinetic parameters of reduction.

EXPERIMENTAL

The investigations were carried out in a H type cell separated by a sintered glass diaphragm. The studies were carried out using LSV and CV with a scan range of +200 mV to -1.0V vs SCE and the voltammograms were recorded using a high sensitivity X-Y recorder. The influence of pH on the reaction was investigated by varying the pH from 1.3 to 5.0 using acetate buffer. The concentration of AM was varied from 2 mM to 10 mM. The sweep rates were varied from 10 mV.s^{-1} to 640 mV.s^{-1}. The products formed at both the peaks were analysed by I.R.& U.V. spectroscopy.

RESULTS AND DISCUSSION

Typical results are presented in Figs. 1 and 2. In the reduction of AM, two reactions are indicated by 2 peaks PC_I and PC_{II} at potentials -40 to -200 mV and around -850 to -900 mV respectively. The shape PC_{II} has been found to be independent of pH whereas PC_I occurs only as a plateau at pH 1.3 and 2.8 which becomes well defined peak at higher pH with a potential shift.

At pH 4.0 and 5.0 on the anodic side two peaks have been observed; Pa_I at -150 to -200 mV and Pa_{II} at -15
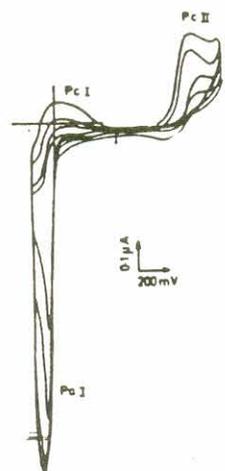

Fig. 1: Cyclic voltammogram of AM sweep rates (mV/s) (1) 20 (2) 80 (3) 160 (4) 320. Concentration AM 1.5 mM, pH 1.3

to -20 mV. Here again both the peaks are found to be dependent on pH. At low pH only Pa_{II} has been observed. Both the cathodic peak potentials are influenced by scan rates. PC_I which occurs as a plateau at 40 mV.s^{-1} turns into well defined peak above 100 mV.s^{-1} and looks like two overlapping peaks in the intermediate region. At pH 4.0, PC_{II} is irreversible. Figure 3 shows the voltammograms with a restricted potential range +150 to -400 mV which shows the characteristics of PC_I clearly. It can be seen from the figure that the peak becomes a well defined one at increasing scan rate and the $PC_I - Pa_I = 30$ mV indicating a two e transfer reaction. It is evident that the reaction at PC_I is under kinetic control. Table I shows the results of PC_I PC_{II}, Pa_I and PA_{II} at different pHs.
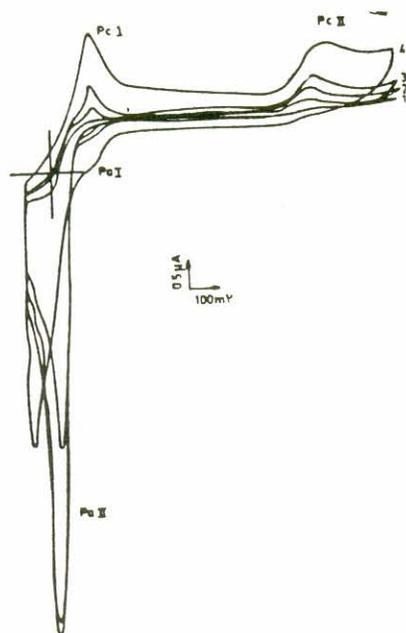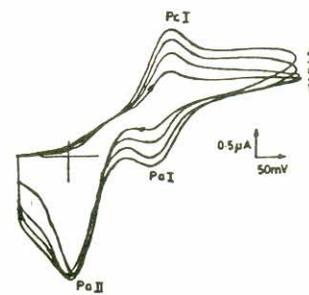
Fig. 2: Cyclic voltammogram of AM at sweep rates (mV/s) (1) 40 (2) 160 (3) 320 (4) 1280. Concentration of AM 6.89 mM; pH 4.0
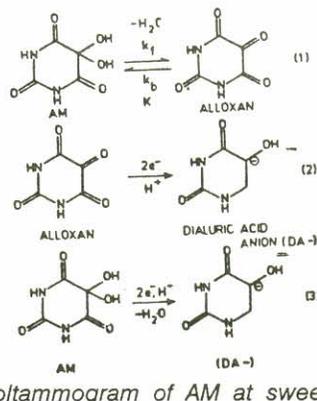

Fig. 3: Cyclic voltammogram of AM at sweep rates (mV/s) (1) 100 (2) 200 (3) 300 (4) 400. Concentration of AM 12.49 mM; pH 4.0

TABLE–I: Values of PC_I, PC_{II}, PA_I and PA_{II} at different pHs

pH	PC_I (mV)	PC_{II} (mV)	PA_I (mV)	PA_{II} (mV)
1.3	Plateau −40mV	−850 to −900	a	+100 to +200
2.8	Plateau −40 mV	−800 10−850	a	0 to +100
4.0	−130 to −140	−880 to −900	−150	−15 to −20
5.0	−200	−100	−200	−20 to −40

Note: "a" indicates absent

The reduction of alloxan is known to proceed in two stages [2]: (1) dehydration of AM (electroinactive) to alloxan (electroactive) followed by reduction to dialuric acid anion (2) depending on the rates of forward and backward reactions, K_f and K_b, the nature of voltammograms varies with change in scan rate. As scan rate increases, the influence of chemical reaction is absent,

then the charge transfer is no longer controlled by the kinetic step. At very high scan rates (say 320 mV.s^{-1}) only a peak is observed which represents the reduction of equilibrium concentration of dehydrated alloxan (pH 4.0 and 5.0). At moderate scan rates, we see the influence of two reactions, the kinetically controlled reduction and the direct reduction of dehydrated alloxan. This is shown by a hump followed by a peak at scan rates like 40 mV.s^{-1}. At low scan rates the reduction is mainly kinetically controlled. Therefore, only a plateau is observed (say 10 mV.s^{-1}).

At pH 1.3 and 2.8, AM exists mainly in the hydrated form. Therefore, K_f is very very small and the equilibrium concentration of dehydrated alloxan is negligible. PC_I occurs as a plateau at all scan rates at low pH.

The equilibrium constant (K) for the dehydration step, the forward and backward rate constants K_f and K_b can be calculated using the equations [3,4].

$$ip = 2.687 \times 10^5 n^{3/2} AD^{1/2} C\nu^{1/2};$$

$$ik = 2.687 \times 10^5 n^{3/2} AD^{1/2} C\nu^{1/2} \times \left(\frac{k}{1+k} \right)$$

$$\text{and} \quad \frac{ik}{ip} = \frac{1}{1.02 + 0.471a/KVl}$$

The calculated values are $K = 0.011$;
$$K_f = 2.978 \times 10^{-3} \text{ s}^{-1};$$
$$K_b = 0.2708 \text{ s}^{-1} \text{ at pH } 4.0$$

At PC_{II} the irreversible reduction of AM to A takes place [3]. The final product has been identified as dialuric acid by U.V. and I.R.

CONCLUSION

The reduction of AM to dialuric acid occurs in two stages namely, the dehydration of AM to A followed by reduction to DA at low pH, whereas at high pH, direct reduction of dehydrated species and reduction of hydrated species compete with each other. The equilibrium constant has been calculated for the dehydration step.

REFERENCES

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