

ELECTROCHEMICAL BEHAVIOUR OF PHENYLGLYOXYLIC ACID ON SILVER CATHODE

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[Received: 1987 July ; Accepted: 1988 January]

Electrochemical reduction of phenylglyoxylic acid on silver cathode was studied in aqueous buffer solutions using voltammetry, cyclic voltammetry, chronoamperometry and controlled potential electrolysis techniques. Voltammetric studies have shown that while two reduction waves are formed around neutral pH, only one wave is formed at acidic and alkaline pH. The two waves are due to the reduction of the carbonyl group present in the phenylglyoxylic acid molecule and phenylglyoxylate anion. Chronoamperometric study has confirmed the cyclic voltammetric data as well as the earlier observations about the reduction of phenylglyoxylic acid which is mixed controlled at acidic pH and diffusion controlled at neutral and alkaline pH. Mandelic acid was the reduction product obtained in the controlled potential electrolysis.

Key words: Voltammetry, phenylglyoxylic acid, electroreduction, silver cathode, mandelic acid

INTRODUCTION

Phenylglyoxylic acid (PGA) is one of the α -ketoacids which has been studied extensively on mercury cathode [1-7]. The effect of pH on the reduction behaviour of PGA shows that single wave is formed in acidic and alkaline pH and two waves are formed in between the pH 6-8. It has been established that the more positive wave is due to the reduction of undissociated phenylglyoxylic acid molecule and the other wave observed at negative potential in alkaline medium is due to the reduction of phenylglyoxylate anion. The reduction of this compound has also been studied on mercury pool cathode in preparative scale [8] and the reported product was mandelic acid. No voltammetric work has been reported for this compound on solid electrodes.

Hence in the present work, an attempt has been made to study the voltammetric behaviour of PGA on silver disc electrode. Rotating disc electrode voltammetry, cyclic voltammetry, chronoamperometry and controlled potential electrolysis techniques have been applied and the experimental results are presented and the possible mechanism of reduction is discussed.

EXPERIMENTAL**Cell**

An H-type glass cell with three electrode assembly was used for all these experiments except for the controlled potential electrolysis. This cell was divided into two compartments by a fine porous glass frit. The working silver disc electrode of diameter 5 mm was connected to the saturated calomel electrode (SCE) acting as reference electrode by a capillary containing agar-agar KCl bridge. Platinum sheet electrode was used as the counter electrode. All the other details of the cell and instrumentation are same as reported earlier [9, 10].

All the chemicals were of analytical grade and double distilled water was used for preparing solutions.

Electrochemical measurements

Electrolytic hydrogen purified by passing through alkaline pyrogallol, concentrated sulphuric acid and double distilled water was passed through the electrolyte for 20 minutes for deaeration as well as for maintaining the inert atmosphere within the cell. The working silver disc electrode tightly inserted into a teflon tube, finished and polished mechanically was used for all experiments except for the controlled potential electrolysis. The above electrode was degreased with trichloroethylene, washed with double distilled water and was positioned into the cell containing solvent supporting electrolyte. Both catholyte and anolyte were the same. All experiments were done at a constant temperature of 298K.

Potentials were applied from a potential scan generator through a potentiostat and the current output was recorded using a fast response x-y recorder. The electrode surface was electrochemically pretreated by cycling between the potential -0.5V to -1.2V vs SCE for a few minutes before actual recording of the current.

Controlled potential electrolysis experiments were done in a divided cell of 300ml capacity. 175ml of the catholyte was used and it was separated by a cation exchange membrane diaphragm. Silver sheet cathode of 20 cm² area was used and the catholyte was stirred by a mechanical stirrer during electrolysis. Anode was platinum. The temperature of the cell was maintained at 298-303K.

Product analysis

Product was identified by paper chromatographic analysis [11] using the reference sample for comparison and it was also confirmed by qualitative and quantitative analysis [12].

RESULTS AND DISCUSSION**Steady state voltammetry**

Fig.1 shows the steady state current potential curve for the reduction of phenylglyoxylic acid on rotating disk electrode (RDE) of silver in aqueous 1M KCl-phosphate buffer of pH 10. Well defined polarographic type limiting wave was obtained under these conditions.

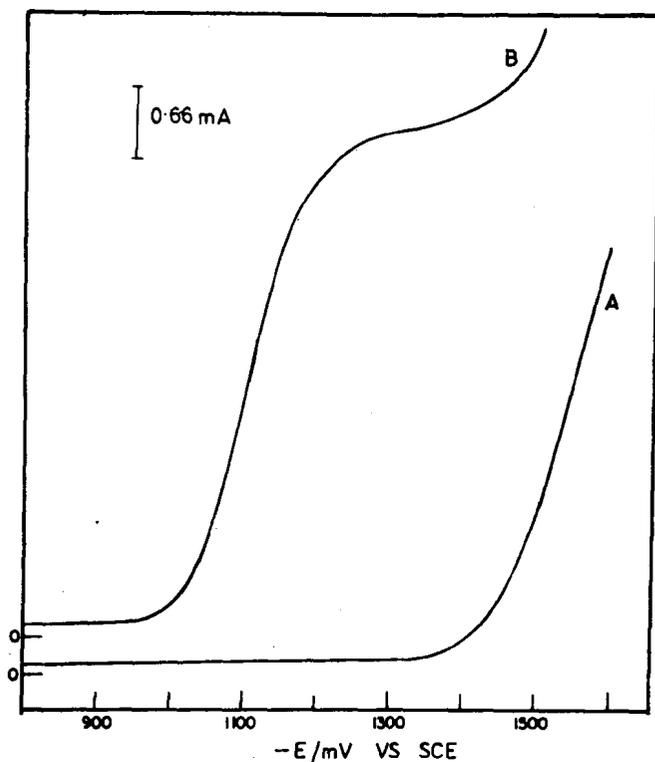


Fig. 1: Steady state current potential curve for the reduction of PGA on Ag disc electrode at pH 10: rpm 850; Temp, 301K (A) 1M KCl - Phosphate buffer only (B) 1×10^{-2} M PGA

Effect of pH

The pH of the electrolyte was varied from 4 to 11. It was found that single wave was obtained at acidic and alkaline pH and two waves were obtained at pH 7.0. The $E_{1/2}$ values were found to increase in the cathodic direction with pH. The limiting current was found to increase slowly up to pH 10 and above that pH slowly decrease. The dependence of current on pH is shown in the form of $\log i$ vs pH in Fig. 2. The reaction order with respect to pH was found to be -0.40 to -0.60.

Effect of rotation rate of the electrode on the limiting current for the reduction of PGA was recorded by varying the rotation speed of the electrode. I_L vs $\omega^{1/2}$ plots were made at pH 4.0 and pH 10.0 and found to be linear.

Effect of concentration

Concentration of phenylglyoxylic acid was varied and the current potential curves were recorded at constant pH and constant rotation of the electrode. The limiting current increased linearly with increase in PGA concentration. The recorded current-potential curves at pH 7 have indicated the formation of two waves and the limiting current for the first wave was very low when compared

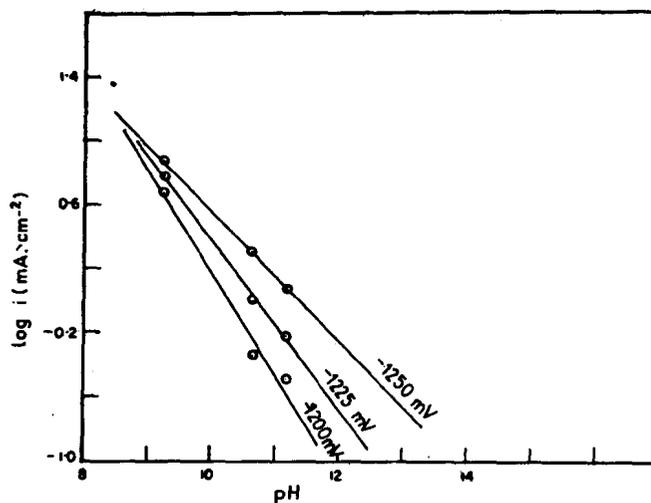


Fig. 2: Dependence of $\log i$ on pH for the reduction of 1.0×10^{-2} M PGA

to the second wave. As the concentration of the PGA increased, the wave height of the first wave decreased and the second wave height increased. Tafel slope values for the current-potential plots in the pH range between 8 and 11.1 were 60 - 70 mV per current decade. Reaction order value was 0.3 to 0.4.

Cyclic voltammetry (CV)

Fig. 3 shows the cyclic voltammograms obtained for the reduction of 9.24×10^{-3} M PGA in 1M KCl - phosphate buffer of pH 10.15. A single well defined peak is observed at -1.125V vs SCE. No anodic wave is observed in the reverse scan. This shows that the reduction process is irreversible.

Effect of pH

CV behaviour of PGA was followed at pH 4.0, 5.0, 5.8, 7.0, 9, 10.15, 11.1, 12.0 and 13.6. The peak current was found to increase slightly with increase in pH and the peak current was maximum at pH 10.15, similar to the observations with RDE. PGA gave single wave (Figs. 3 and 4) except around neutral pH (Fig. 5) where two waves were observed. No anodic peak was observed on reverse scan on all pHs.

Peak potential E_p and half peak potential $E_{p1/2}$ recorded at different pH conditions are presented in Table I. E_p and $E_{p1/2}$ were found to increase linearly with increase in pH in the cathodic direction both in acidic and alkaline pH range and the shift was found to be 37mV per pH unit. This observation suggests that protonated carbonyl group of the molecule is involved in the electron transfer reaction.

Effect of sweep rate

Cyclic voltammograms were recorded for the reduction of PGA at different sweep rates under different pH conditions (Figs. 4 and 5).

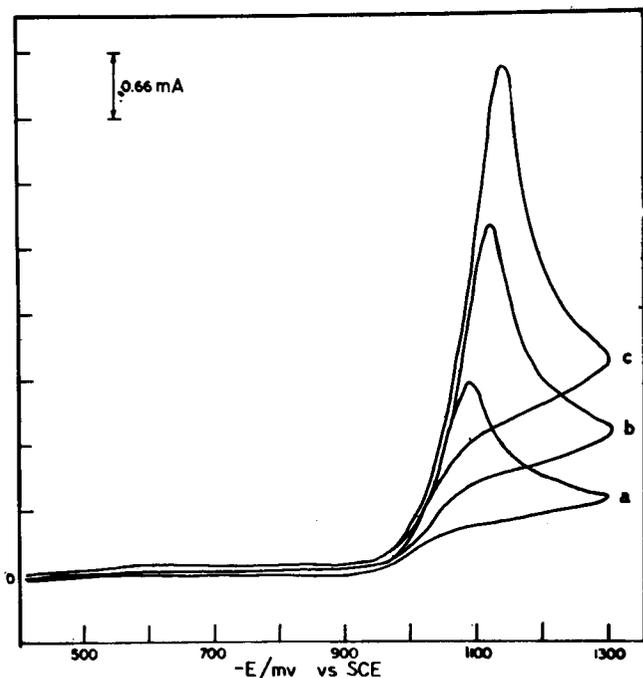


Fig.3: Cyclic voltammograms of PGA on Ag disc electrode at pH 10.15 at sweep rate 300 mV s^{-1} ; PGA concn: (a) $4.62 \times 10^{-3} \text{ M}$; (b) $9.24 \times 10^{-3} \text{ M}$; (c) 1.386×10^{-2}

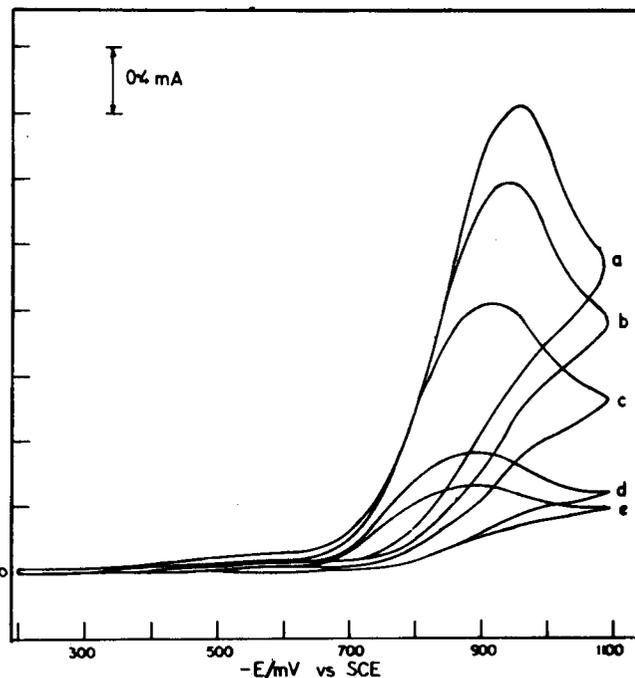


Fig.4: Cyclic voltammograms of PGA ($9.24 \times 10^{-3} \text{ M}$) on Ag disc electrode pH 4 for different sweep-rates (mV.s^{-1}): (a) 450 (b) 300 (c) 150 (d) 30 (e) 15

TABLE-I: Dependence of E_p and $E_p^{1/2}$ values on pH for the reduction of phenyl glyoxylic acid ($9.24 \times 10^{-3} \text{ M}$) at silver disc electrode.

Electrolyte	E_p vs SCE (mV)	$-E_p^{1/2}$ vs SCE (mV)
4.0	955	815
5.0	975	855
5.8	1025	945
7.0	1080	985
9.0	1120	1060
10.15	1125	1070
11.10	1215	1135
12.10	1260	1190
13.60	1295	1225

Fig.6 shows the peak current i_p vs $V^{1/2}$ plots for the reduction of PGA at four different pH conditions. The peak current i_p was linear with $V^{1/2}$ and the current function values, $i_p/ACV^{1/2}$ were found to be constant in the pH range 4 - 12.1. These observations have indicated that the reduction process is diffusion controlled in the above pH range.

Peak potential was found to shift in the cathodic direction with sweep rate throughout the pH range studied. Dependence of E_p on $\log V$ for the reduction of PGA at pH 5.8 and 10.1 is shown in Fig.7.

E_p was found to vary linearly with $\log V$ up to a sweep rate of 45 mV s^{-1} and afterwards steep increase in peak potential with sweep rate was observed. The slope of $d E_p / d \log V$ was found to be 30 mV per decade change of sweep rate at lower sweep rates with pH 10.1. The shift in E_p values in the cathodic direction with sweep rate has shown that the reduction process is irreversible in character.

Effect of concentration

The peak current of the single wave formed at pH below 6 and above 8 was found to increase linearly with increase in concentration of PGA. The peak potential, E_p , was found to shift in the cathodic direction with increasing concentration of PGA. It is probable that adsorption of reactant might have blocked the electrode surface. Such effects on CV behaviour have been predicted theoretically [13,14] and also observed experimentally for other reactions [15,16].

Chronoamperometry

This technique was used to derive more information about the

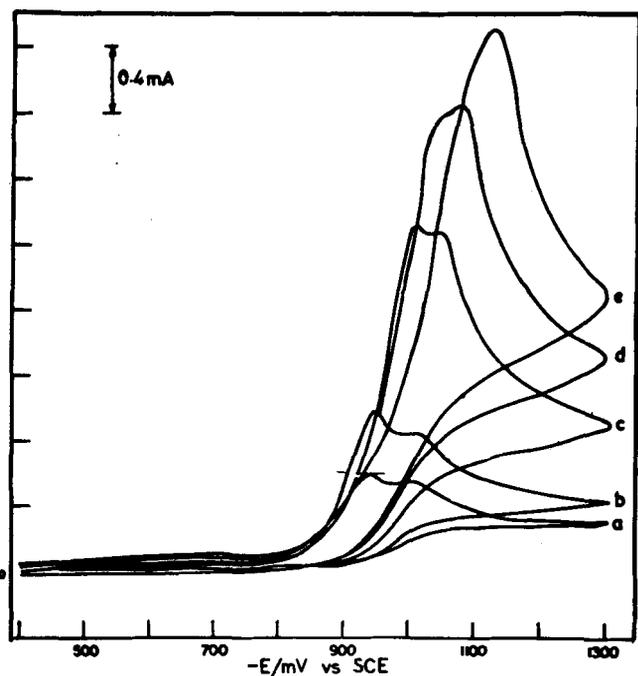


Fig.5: Cyclic voltammograms of $9.24 \times 10^{-3} \text{M}$ PGA on Ag disc electrode at pH 7.0 at various sweep rates (mv.s^{-1}) (a) 15 (b) 30 (c) 150 (d) 300 (e) 450

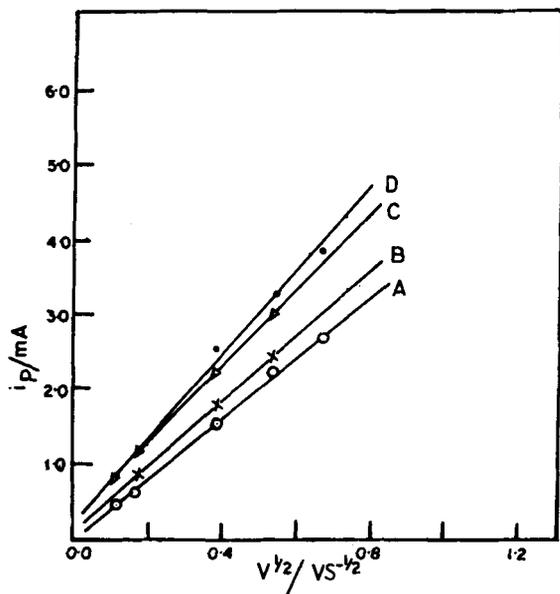


Fig.6: Plot of i_p vs $V^{1/2}$ for the reduction of $9.24 \times 10^{-3} \text{M}$ PGA at different pH: Temp. 293 K; pH(a) 4.0 (b) 5.8 (c) 12.1 (d) 9.0

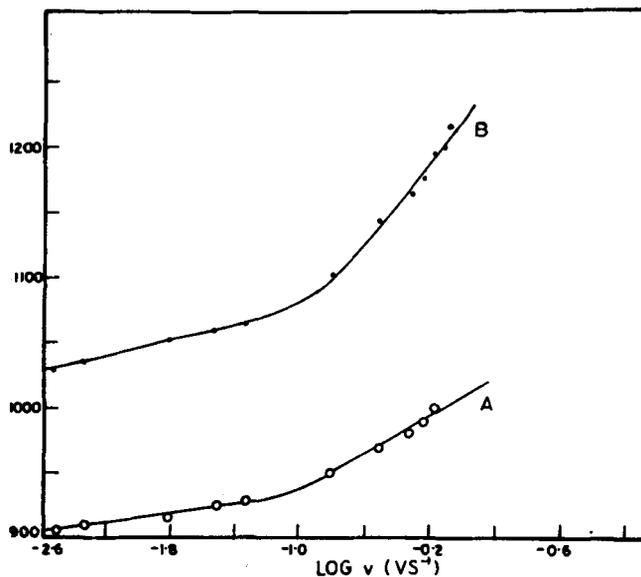


Fig.7: Dependence of E_p on $\log V$ for the reduction of PGA ($9.24 \times 10^{-3} \text{M}$) (a) pH 5.8 (b) pH 10.1

nature of control of electrode process. From the current – time curves recorded at different pH, current I versus $t^{-1/2}$ plots were derived (Fig.8). I vs $t^{-1/2}$ plots were linear for the whole range of transient. This information has confirmed that the process is diffusion controlled.

Controlled potential electrolysis

Experiments were done in a divided cell for the reduction of PGA at controlled potential under different pH conditions in a stirred solution. 20 cm^2 area of silver sheet was used as cathode. After the electrolysis, the solution was analysed. Product was identified and estimated. Mandelic acid was the product formed in these experiments, thereby revealing that phenylglyoxylic acid undergoes two electron reduction.

The reduction of PGA on silver electrode in aqueous medium has indicated that at the limiting current region the reduction behaviour is similar to the polarographic behaviour reported in the literature and the two waves observed around neutral pH are due to the reduction of molecular form of PGA and the corresponding carboxylate anion. In the pH range 4 - 12 the overall reduction process occurring at the limiting current region is found to be diffusion controlled.

Reduction mechanism occurring at the foot of the wave in alkaline medium

The following results are obtained from the various electroanalytical techniques used in this study:

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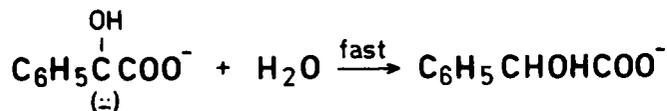
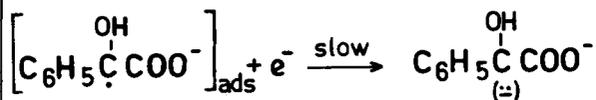
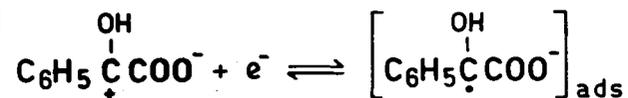
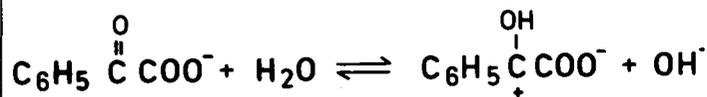
(i) The overall reaction yields mandelic acid as two electron reduction product.

(ii) The Tafel slope value is 60-70 mV; this value is supported by the plot of E_p vs $\log V$ giving 30 mV slope which corresponds to the Tafel slope value of 60 mV. This shows that the first electron transfer is reversible.

(iii) Reaction order values with respect to PGA and protons are found to be fractional, which indicates that Temkin type of adsorption occurs over the electrode surface. The elevated slope values of the E_p - $\log V$ plot (Fig.7) at higher sweep rates, the shift of E_p in the cathodic direction with increasing concentration of the reactant observed in CV study support the adsorption behaviour.

(iv) $E_{1/2}$ and $E_{p1/2}$ values are found to shift in the cathodic direction with increasing pH of the solution (Table I). This observation suggests that protonated carbonyl group of PGA may be involved in the electron transfer reaction.

Therefore, phenylglyoxylic acid reduction of silver electrode in aqueous alkaline medium may take the following reaction pathway. Reduction of phenylglyoxylate anion:



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