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REDUCTION OF PHENYLGLYOXYLIC ACID ON SILVER CATHODE IN DIMETHYL FORMAMIDE

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The electrochemical reduction of potassium phenylglyoxylate was studied at a silver disc electrode in dimethylformamide medium using cyclic voltammetry. Only one irreversible reduction wave at high negative potential (-1.6V vs SCE) was observed. The effect of the presence of proton donors and n-butyl bromide on the voltammetric behaviour of potassium phenylglyoxylate was also studied to understand the reduction mechanism in aprotic medium. The appearance of one additional irreversible cathodic wave at less negative potential in the presence of proton donors without affecting the original wave and enormous increase in the wave height of the original wave as well as the additional wave in the presence of n-butyl bromide have indicated the formation of radical anions in both the waves. These observations have confirmed that the original wave was due to the one electron reduction of phenylglyoxylate anion which was followed by dimerization and the additional wave observed in the presence of limited amount of protons was due to the one electron reduction of phenylglyoxylic acid molecule.

Key words: Phenylglyoxylic acid, silver cathode, nonaqueous medium, cyclic voltammetry

INTRODUCTION

The polarographic reduction of phenylglyoxylic acid in aqueous solution has been studied by several workers [1-7]. The reduction of this compound has also been studied [8] on mercury pool cathode in preparative scale and the reported product is mandelic acid. All these studies have clearly established that phenyl glyoxylic acid gives two waves around neutral pH and single wave both in acidic and alkaline pH. The above observation has been explained by the reduction of phenylglyoxylic acid molecule and phenylglyoxylate anion at two different potentials.

The cyclic voltammetric study [9] on the reduction of phenylglyoxylic acid in aqueous medium on silver electrode has also confirmed the above facts and the electrochemical reduction process is found to be diffusion controlled in the pH range 4-11 and the peak current is maximum at pH 10.15.

In this paper the results of the investigation on the electrochemical reduction behaviour of potassium phenylglyoxylate in nonaqueous medium are presented, with the aim to study the possibility of the formation of phenyl substituted tartaric acid by the dimerization of the radical intermediates expected to be formed during reduction.

EXPERIMENTAL

Chemicals

Laboratory grade dimethylformamide was dried under anhydrous copper sulphate, twice distilled and used. Potassium phenylglyoxylate was prepared by neutralising the analytical grade phenyl glyoxylic acid with pure potassium hydroxide solution and isolated the salt by evaporation, dried and used. Analytical grade sodium perchlorate was dried under vacuum and used.

Cell

A H-type glass cell with three electrode assembly was used in the present cyclic voltammetric study. The cathode and anode compartments were separated by a fine porous glass frit. The working electrode was connected to the saturated calomel electrode (SCE) by a capillary containing agar-agar- KCl. All the other details of the cell and instrumentation are same as reported earlier [10,11].

Electrochemical measurements

Electrolytic hydrogen gas was used for deaeration after purifying the gas by passing through heated copper foils (523K), column containing A-4 type molecular sieves and wash bottle containing the same solvent supporting electrolyte (SSE). The working silver disc electrode of 0.5 cm diameter was inserted into the teflon tube and finished mechanically. It was degreased with trichloroethylene and was positioned into the cell containing SSE. Platinum foil was used as the counter electrode. Both catholyte and anolyte were the same.

Potentials were applied from a potential scan generator through a potentiostat and the current output was recorded using a fast response X-Y recorder. Purified hydrogen gas was passed through catholyte for twenty minutes and 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.

RESULTS AND DISCUSSION

Voltammetric behaviour of potassium phenyl glyoxylate in DMF containing 0.2M $NaClO_4$

The cyclic voltammograms were recorded for the reduction of potassium phenylglyoxylate in DMF containing 0.2M $NaClO_4$ on a stationary silver disc electrode (Fig. 1). Only one cathode wave at high negative potential (-1.60V vs SCE) was observed in the cathodic scan and no complimentary anodic wave was observed in the reverse scan even at sweep rate upto 1 $V.s^{-1}$. The sweep rate was varied from 50 mV. s^{-1} to 500 $mV.s^{-1}$ and the effect of sweep rate on the peak current and peak potential was recorded (Fig.1). The peak current was found to increase linearly at lower sweep rates and less linearly at higher sweep rates (Fig.2). The earlier study

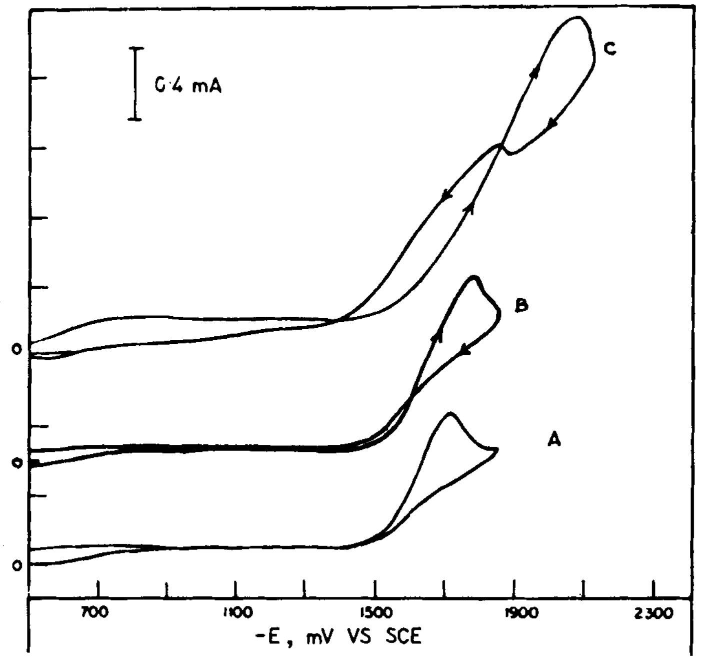


Fig. 1 Cyclic voltammograms of potassium phenylglyoxylate (1 x 10^{-2} M) at silver disc electrode in DMF/0.2M $NaClO_4$, temp. 298K, scan rate (A) 50 mV s^{-1} (B) 100 mV s^{-1} (C) 500 mV s^{-1}

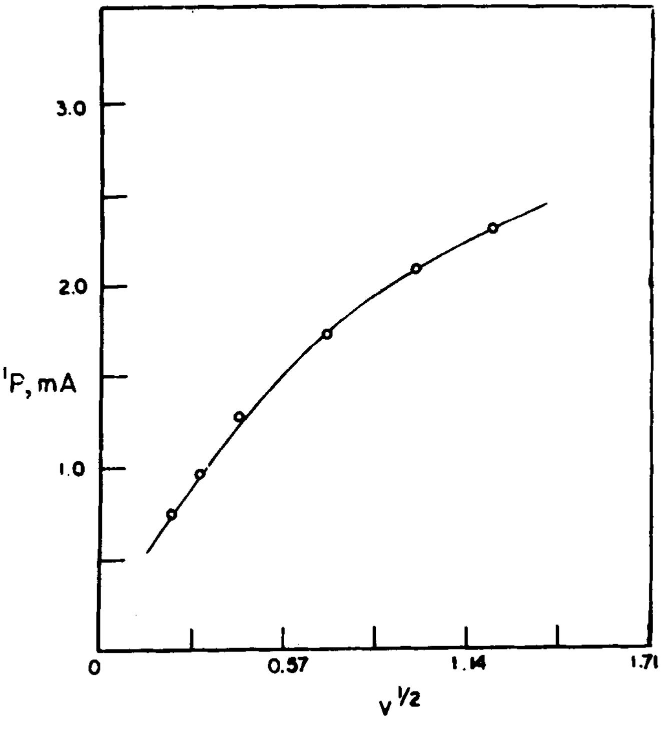


Fig. 2: Plot of i_p vs $v^{1/2}$ for the reduction of potassium phenylglyoxylate (1 x 10^{-2} M) in DMF/0.2 M $NaClO_4$

of the reduction of phenylglyoxylic acid in aqueous medium on mercury pool cathode [8] has shown that the reduction is a two electron process and product is mandelic acid. The cyclic voltammetric study of the system in aqueous medium on the same silver disc electrode has revealed that the single peak with maximum current obtained at pH 10 for the same concentration and sweep rate was more than twice the value of the peak current obtained in this present study in DMF. This is an indirect evidence that the wave obtained in the reduction of potassium phenylglyoxylate in DMF may be a one electron process with the formation of radical anion.

The peak potential was found to shift in the cathodic direction with sweep rate and there was a sharp increase in the peak potential values at higher sweep rates as shown in Figs. 3 and 1.

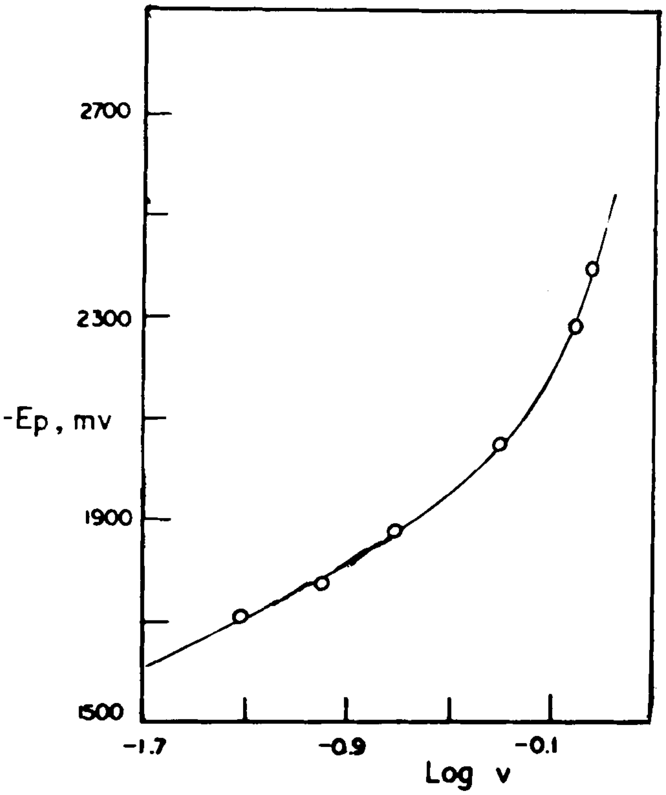


Fig. 3: Plot of E_p vs log V for the reduction of potassium phenylglyoxylate (1 x 10^{-2}M) in DMF/0.2 M $NaClO_4$

The enormous shift in peak potential at higher sweep rates may be due to the change in adsorption mechanism. The observed shift of peak potential in the cathodic direction and the absence of anodic peak in the reverse scan have suggested that the overall process is an irreversible process.

At higher sweep rates (> 100 mV. sec^{-1}) the voltammetric curve on the reverse sweep is found to cross over the forward sweep curve as shown in Fig. 1B and 1C. This may either be due to the activation of the electrode surface at extreme cathodic potentials, alkali metal ion discharge and film formation on the silver electrode or due to regeneration of electroactive species by autocatalytic reaction [12, 13]. The present experimental data are insufficient to distinguish between these possibilities.

Influence of other additives

To gain further insight into the reaction mechanism, a number of proton donors and n-butylbromide were added to the above system and their influence on the voltammograms were recorded.

When water was added as a mild protonating agent, an additional cathodic wave at less negative potential (-1.2 V vs SCE) was observed (Fig. 4) in addition to the original wave.

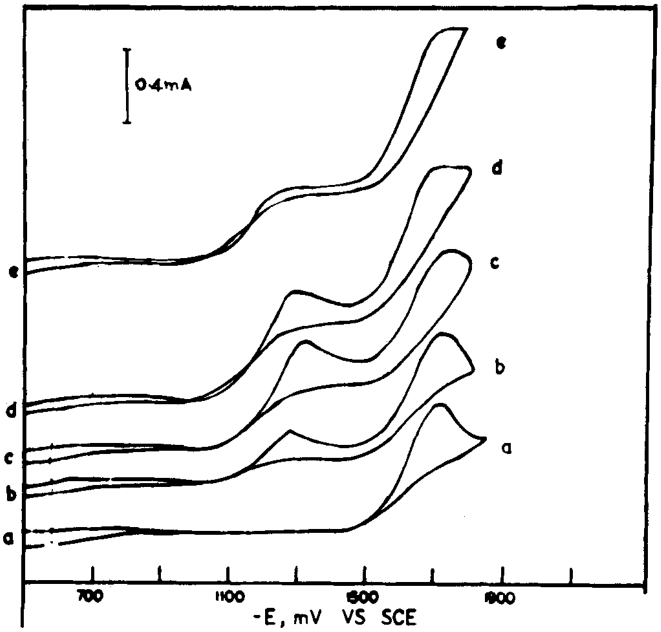


Fig. 4: Cyclic voltammograms of potassium phenylglyoxylate (1 x 10^{-2} M) in DMF/0.2 M $NaClO_4$ in presence of different concns of water. Scan rate 50 mV s^{-1}: (a) 0M; (b) 0.277M (c) 0.554M (d) 1.385M (e) 2.216M

As the water addition was increased, the wave height of the new wave also increased without affecting the original wave. If the additional wave is assumed to be due to the reduction of protonated carbonyl group of potassium phenyl glyoxylate, the usual behaviour would be to increase the wave height of the additional wave at the expense of the original wave and the wave height of the additional wave would be doubled and the original wave would have disappeared. The fact that the additional wave observed in the presence of water has not affected the original wave, indicates that in presence of water two different reactive species are involved in the formation of two waves. Addition of phenol as protonating agent was also studied and similar effect but less pronounced was observed.

Cyclic voltammetric behaviour of potassium phenylglyoxylate was also studied in presence of n-butyl bromide and its effect on the voltammograms was recorded both in the presence and absence of water as protonating agent. The wave height of original wave observed in pure DMF increased in the presence of n-butyl bromide. Fig. 5 shows the voltammograms recorded for the reduction of potassium phenylglyoxylate containing 0.138M water in presence of different concentrations of n-butyl bromide at 50mV s-1.

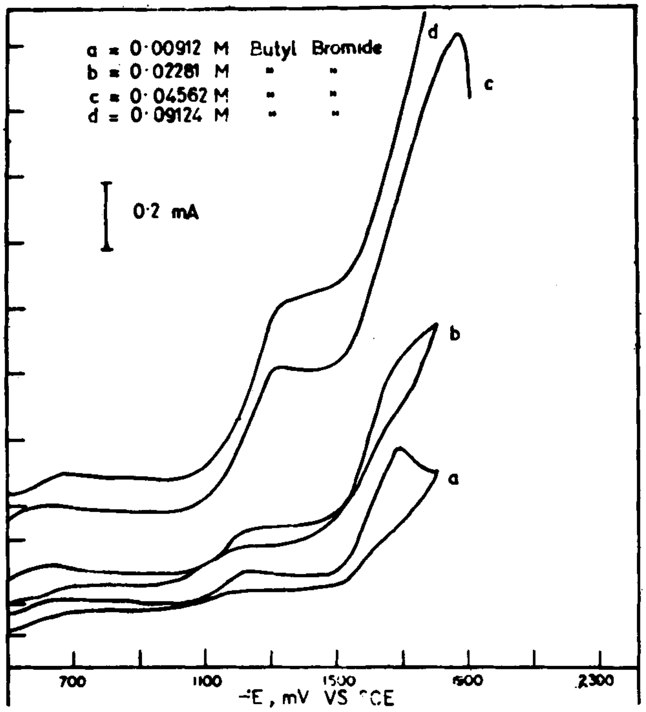


Fig. 5: Cyclic voltammograms of potassium phenylglyoxylate (0.6 x 10^{-2}M) in DMF/0.2 M $NaClO_4$ in presence of 0.138 M water and different concns. of n-butylbromide. Scan rate 50 mV.s^{-1}

It was also found that the wave height of both the waves increased enormously as the addition of n-butyl bromide was increased. As n-butyl bromide is known to be reduced by the radical anion with the instantaneous regeneration of the reactant in the vicinity of the electrode [14] (as shown in equation below) the enormous increase in the wave height is expected

$$A + e^- \rightleftharpoons A^{\cdot -}$$

$$A^{\cdot -} + BX \rightleftharpoons A + BX^{\cdot -}$$

$$BX^{\cdot -} \longrightarrow B^{\cdot} + X^-$$

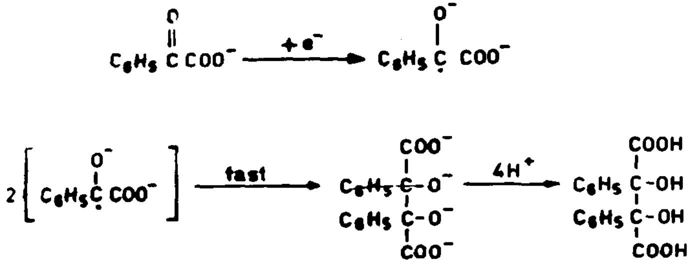
$$A^{\cdot -} + B^{\cdot} \rightleftharpoons A + B^- \xrightarrow{H+} A + HB$$

The observed fact that the wave height of both the waves increased enormously has suggested that the intermediate species formed in both the wave formations have reacted with the n-butyl bromide. This is a clear indication that two different reactants are involved in the formation of two waves and radical anions are found to be the intermediate species in both the cases.

The present cyclic voltammetric study of the reduction of potassium phenylglyoxylate on silver electrode in nonaqueous medium in presence of addition agents like water and n-butyl bromide has confirmed the earlier literature that phenyl glyoxylate is in equilibrium with phenylglyoxylic acid in presence of water and both the species are electroactive at different potentials. In the present study the original wave was due to the reduction of phenyl glyoxylate anion and the additional wave observed in presence of water was due to the reduction of phenyl glyoxylic acid molecule as shown in the reaction Scheme I.

$$\begin{tikzcd}
C_6H_5\,COCOOH \arrow[r, "2H^+", "2e^-"'] \arrow[d, shift left, "+H^+"] & C_6H_5\,CHOHCOOH \arrow[d, shift left, "+H^+"] \\
C_6H_5\,COCOO^- \arrow[r, "2H^+", "2e^-"'] \arrow[u, shift left, "-H^+"] & C_6H_5\,CHOHCOO^- \arrow[u, shift left, "-H^+"]
\end{tikzcd}$$

In conclusion, it has been found that phenylglyoxylate anion in pure dimethyl formamide undergoes one electron reduction on silver cathode with the formation of the radical anion which subsequently undergoes fast dimerization reaction thus leading to phenyl substituted tartaric acid as follows:



$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}COO^- \xrightarrow{+e^-} C_6H_5\overset{\overset{\displaystyle O^-}{|}}{\dot{C}}\;COO^-$$

$$2\left[C_6H_5\overset{\overset{\displaystyle O^-}{|}}{\dot{C}}COO^-\right] \xrightarrow{\text{fast}} \begin{array}{c} COO^- \\ | \\ C_6H_5\,C-O^- \\ | \\ C_6H_5\,C-O^- \\ | \\ COO^- \end{array} \xrightarrow{4H^+} \begin{array}{c} COOH \\ | \\ C_6H_5\,C-OH \\ | \\ C_6H_5\,C-OH \\ | \\ COOH \end{array}$$

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