JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) · SHORT COMMUNICATION

SHORT COMMUNICATION

Production of tartrate and glycolate from the electrochemical reduction of glyoxylate

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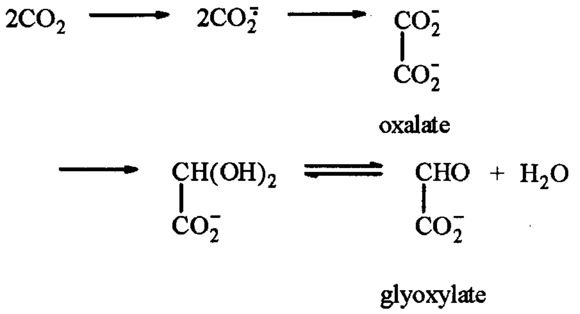
Received 3 February 1993; revised 9 June 1993

1. Introduction

Glyoxylic acid is an important electrochemical product from oxalic acid [1]. The electrochemical reduction of oxalic acid has been studied by a number of workers [2, 3] including ourselves [4]. We have shown that it can also be formed directly from carbon dioxide by electrochemical reduction at pH 9–10 in the presence of tetraalkylammonium salts on mercury and on glassy carbon [5, 6]:



$$2CO_2 \longrightarrow 2CO_2^{\cdot-} \longrightarrow \begin{array}{c} CO_2^- \\ | \\ CO_2^- \end{array}$$

oxalate

$$\longrightarrow \begin{array}{c} CH(OH)_2 \\ | \\ CO_2^- \end{array} \rightleftharpoons \begin{array}{c} CHO \\ | \\ CO_2^- \end{array} + H_2O$$

glyoxylate

There has been considerable controversy about these reductions. Bewick and Greener [7, 8] claimed to have produced glycolic acid from CO_2 on lead and malic acid from CO_2 on mercury but they did not detect glyoxylic acid. Similar results were reported by Wolf and Rollin [9] but others were unable to repeat these results, or obtained different products [3].

A number of workers have studied the voltammetric reduction of glyoxylic acid [10, 11]. But there have been no direct preparative studies since Bauer [12] in 1931. Some preparative studies are presented here.

It has been generally assumed that the electrochemical reduction of glyoxylate goes by a two electron process to give glycolate (perhaps explaining Bewick's results [7]). However another possibility exists: the formation of tartaric acid by a one-electron reduction followed by a dimerisation (pinacol formation).

Further reduction of tartaric acid could lead to malic acid (as claimed by Bewick [8] and Wolf [9]). We observed an HPLC peak from the reduction products of the reduction of oxalic acid which could be attributable to malic acid [4].

2. Experimental details

Voltammograms were run on a Bioanalytical Systems CV1A voltammeter. Controlled potential electrolyses were carried out with a Witton T6 Tutorial Potentiostat.

The cell for voltammetry was a 100 cm^3 beaker fitted with a three-hole stopper. Working electrodes for voltammetry were a lead inlaid disc (area 0.354 cm^2), a glassy carbon inlaid disc (area 0.395 cm^2) and a hanging mercury drop (area 0.0136 cm^2). The lead and carbon electrodes were both polished before each run. The reference electrode was a saturated calomel electrode and the counter electrode a platinum foil electrode. Solutions were made up of glyoxylic acid (0.1 M) and tetramethylammonium tetrafluoroborate (0.1 M) in deionized water. The pH was adjusted with tetramethylammonium hydroxide to the required value. The high concentration of glyoxylic acid acts as its own buffering agent. Even for voltammetric experiments the high concentration is required as most of the glyoxylate is in the hydrated electroinactive form [10, 12]. The pH values used were 2.1, 7.0 and 9.0. Similar solutions were made up for the controlled potential electrolyses. All solutions were deaerated with oxygen-free nitrogen for 15–20 min before electrolysis.

Controlled potential electrolyses were carried out with a graphite disc electrode in a Perspex dialysis cell (area 19.6 cm^2) or the same cell with a pure lead sheet (0.1 mm thick, area 19.6 cm^2) inserted between the two sections of the cell. The compartments were separated by a cation exchange membrane. A silver–silver chloride reference electrode and a platinum foil counter electrode were used. The catholyte volumes were 75 cm^3 with carbon in the cell and 65 cm^3 with lead.

A mercury pool electrode (area 75.6 cm^2) was arranged in a two compartment cell, again each compartment being separated by a cation exchange membrane. A saturated calomel reference electrode and a platinum foil counter electrode were used. The catholyte volume was 250 cm^3.

A rotating stirrer was fitted in each cell. At intervals from half-hourly up to two hourly samples (2 cm^3) were removed. Each was passed separately through an ion exchange column to remove tetramethylammonium ions. The eluate from each sample was collected and made up to 25 cm^3 in a standard flask and subjected to separate analysis by HPLC on an Altex Model 30 Isocratic Liquid Chromatograph using a 300 mm × 7.8 mm Aminex

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Table 1. Voltammetric data for glyoxylic acid in neutral tetramethylammonium tetrafluoroborate (0.1 M). Sweep rate 60 mV s^{-1}, i_p/A = peak current density

Electrode	*Electrode area*/cm^2	E_p /V vs SCE	i_p/A /mA cm^{-2}	αn_a
Carbon	0.395	−1.31	1.00	0.1
Lead	0.354	−1.64	6.47	0.3
Mercury	0.0136	−1.61	5.54	0.3

HPX-87 column and a Pye Unicam PU 4020 u.v. detector set to 210 nm, eluting with 0.016 M H_2SO_4.

Electrolysis was continued until approximately 90% of the glyoxylate was consumed. The total electrolysis times for each run varied from 2.5–8.5 h (lead) to 6.25–12.3 h (mercury) and 13.25–14.0 h (carbon). The current was monitored regularly to obtain the average current during each period before sampling.

3. Results

Voltammetric studies were carried out at each electrode to determine the appropriate potential for controlled potential electrolyses. Data are shown in Table 1. Controlled potential electrolysis was carried out in the three compartment cell at pH 2.1, 7.0 and 9.0 for each electrode with an applied potential 0.2 V cathodic of the observed voltammetric peak potentials. The results are summarized in Tables 2 and 3.

Observed current efficiencies were 50–60% under all conditions. Generally current density decreased on lead and mercury at pH 7 and 9 (for example from 7.29 to 5.36 mA cm^{-2} on lead at pH 9 over 2.5 h), but remained constant at about 1.3 mA cm^{-2} on carbon at these pH values over 13 h. However at pH 2.1 on all electrodes there was a noticeable increase (for example 3.78–5.82 mA cm^{-2} on lead over 8.5 h). On mercury current densities were in the range 1.1–1.7 mA cm^{-2} at pH 7 and 9.

Under most conditions the observed products were glycolate, tartrate and some formate and oxalate. No malate was detected. In acid conditions (pH 2.1) over 90% of the product was glycolate. Tartrate was present as about two thirds of the detected products at pH 7 and 9 on both lead and mercury. On carbon very little tartrate was formed at any pH. Small amounts of formate were found with carbon and mercury but not with lead at most pH's. Some oxalate was also formed in all cases (0.1–8.4%). The product yields shown in Table 3 are those analysed from samples taken at the maximum electrolysis times shown in Table 2.

Graphs were plotted of log [concentration of glyoxylate] against time, which showed a linear decrease over times up to 18 h indicating pseudo first order kinetics. Rate constants, normalized for electrode area, are shown in Table 3.

4. Discussion

The product distribution varied greatly depending on the conditions. At pH > 7 on metal electrodes when the glyoxylic acid exists mainly as the anion, tartaric acid was the major product. At the relatively positive potentials used there was no evidence of malate formation as reported by Bewick [8] and by Wolf [9]. But Bewick used a potential of −2.6 V on mercury. That used by Wolf was not reported.

Zuman [13] studied the polarography of carbonyl compounds and found one-electron waves in alkaline solutions, but two-electron waves in acid. Saveant [14] and Parker [15] have observed the reduction of benzaldehyde on mercury ($E_{1/2} = -1.61$ V). They found the product to be a pinacol dimer in basic ethanol and in aqueous alcohol. Parker considers that in basic solution the predominant mechanism is one involving dimerisation of the benzaldehyde anion radical, although in neutral and acid solutions, protonation of the radical anion

Table 2. Controlled potential electrolysis of glyoxylic acid in aqueous 0.1 M tetramethylammonium tetrafluoroborate

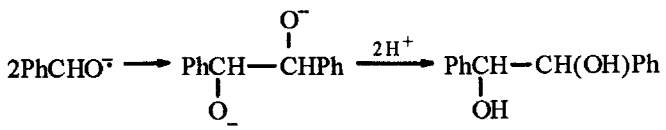
Electrode	*Electrode Area*/cm^2	*Electrolysis potential*/V	*pH*	*Current density* /mA cm^{-2}	*Current efficiency*	*Electrolysis time*/h	*Coulombs* /10^3
Carbon	19.6	−1.46	2.1	2.53	48	14.0	2.5
			7.0	1.22	55	13.25	1.14
			9.0	1.31	63	13.25	1.22
Lead	19.6	−1.85	2.1	5.9	46	8.5	3.54
			7.0	4.75	54	3.0	1.01
			9.0	5.4	50	2.5	0.95
Mercury	75.6	−1.80	2.1	1.07	46	12.3	3.58
			7.0	1.14	55	6.25	1.94
			9.0	1.62	58	8.0	3.53

Table 3. Electrolytic reduction products from glyoxylic acid and rate constants (*k*)

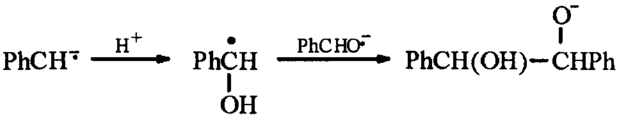
Electrode	*pH*	*Glycolate*		*Tartrate*		*Formate*		*Oxalate*		$k/10^{-6}$ $/\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$
		/mM	/%	/mM	/%	/mM	/%	/mM	/%	
Carbon	2.1	63.7	97.3	0.89	1.4	0.46	0.3	0.69	1.1	7.35
	7.0	48.9	84.6	0.0	0.0	4.0	6.9	4.88	8.4	10.5
	9.0	55.1	84.8	4.4	6.8	3.77	5.8	1.68	2.6	9.4
Lead	2.1	85.0	94.7	4.7	5.2	0.0	0	0.1	0.1	33.4
	7.0	15.8	34.1	30.4	65.7	0.0	0	0.09	0.2	63.3
	9.0	16.5	34.3	31.4	65.3	0.0	0	0.15	0.3	50.3
Mercury	2.1	41.6	95.9	1.68	3.9	0.0	0	0.08	0.2	1.60
	7.0	15.4	36.1	25.6	60.0	1.44	3.4	0.26	0.6	4.88
	9.0	16.4	31.4	34.2	65.4	1.5	2.9	0.17	0.3	4.97

precedes dimerization:

$$\mathrm{PhCHO} + e^- \rightleftharpoons \mathrm{PhCHO}^{\cdot-}$$

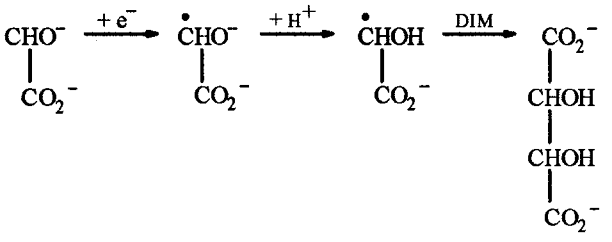


$$2\mathrm{PhCHO}^{\cdot-} \longrightarrow \mathrm{Ph}\underset{\mathrm{O}^-}{\mathrm{CH}}-\overset{\mathrm{O}^-}{\mathrm{C}}\mathrm{HPh} \xrightarrow{2\mathrm{H}^+} \mathrm{Ph}\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH(OH)Ph}$$



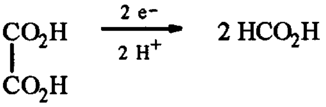
$$\mathrm{PhCH}^{\cdot-} \xrightarrow{\mathrm{H}^+} \mathrm{Ph}\underset{\mathrm{OH}}{\overset{\bullet}{\mathrm{C}}}\mathrm{H} \xrightarrow{\mathrm{PhCHO}^{\cdot-}} \mathrm{PhCH(OH)}-\overset{\mathrm{O}^-}{\mathrm{C}}\mathrm{HPh}$$

Glyoxylate is likely to behave in an analogous manner with perhaps the protonation–dimerization route being favoured because of the existing carboxylate negative charge:



$$\begin{array}{c}\mathrm{CHO^-}\\ | \\ \mathrm{CO_2^-}\end{array} \xrightarrow{+e^-} \begin{array}{c}\overset{\bullet}{\mathrm{CHO^-}}\\ | \\ \mathrm{CO_2^-}\end{array} \xrightarrow{+\mathrm{H}^+} \begin{array}{c}\overset{\bullet}{\mathrm{CHOH}}\\ | \\ \mathrm{CO_2^-}\end{array} \xrightarrow{\mathrm{DIM}} \begin{array}{c}\mathrm{CO_2^-}\\ | \\ \mathrm{CHOH}\\ | \\ \mathrm{CHOH}\\ | \\ \mathrm{CO_2^-}\end{array}$$

The formation of formate especially on carbon is unexpected. It is likely to be due to the presence of small amounts of oxalate impurity in the reagent grade glyoxylic acid (detected by HPLC), which is commonly found. Oxalic acid can be reduced by a two electron step to formate [4]:



$$\begin{array}{c}\mathrm{CO_2H}\\ | \\ \mathrm{CO_2H}\end{array} \xrightarrow[2\,\mathrm{H}^+]{2\,e^-} 2\,\mathrm{HCO_2H}$$

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