KINETIC CONTROL AND ADSORPTION IN THE VOLTAMMETRY OF GLYOXYLATE

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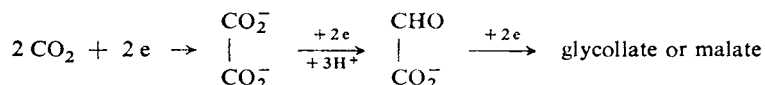
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Linear sweep voltammetry of glyoxylate on a stationary mercury electrode showed strong adsorption effects in addition to kinetic control because of the hydration of the aldehyde groups. The methods of Shain were used to minimise the adsorption and to determine the kinetic function at pH 9·0. The dehydration rate constant was found to be $1·14 \pm 0·03 \ s^{-1}$.

Glyoxylate is an important component of various biological metabolic processes[1]. It is also a key intermediate in the oxalate route for the electrochemical reduction of carbon dioxide[2].

$$2 \ CO_2 + 2 \ e \ \rightarrow \ \begin{matrix} CO_2^- \\ | \\ CO_2^- \end{matrix} \ \xrightarrow[+3H^+]{+2e} \ \begin{matrix} CHO \\ | \\ CO_2^- \end{matrix} \ \xrightarrow{+2e} \ \text{glycollate or malate}$$

The first step from carbon dioxide to oxalate is known[2,3] to occur in solutions of low proton availability. It has been well established[4-7] that glyoxylate may be formed by the electrochemical reduction of oxalic acid in aqueous acid solutions. We have shown that in alkaline solutions carbon dioxide may be converted directly to glyoxylate on a glassy carbon electrode[2,8]. As a part of our studies on carbon dioxide fixation[2,8] we are therefore making a more detailed study of the electroreduction of glyoxylate. The product on mercury is likely to be malic acid as previously reported by others[9,10].

Previous studies[11,12] on the polarography of glyoxylate indicated that the wave was kinetically controlled by the slow dehydration of the hydrate in the manner of formaldehyde. Polarographic measurements[12] have been made to determine the equilibrium constant for the dehydration. Temperature jump measurements[13] have been made of the dehydration rate constants.

We used linear sweep voltammetry at a stationary mercury electrode to determine $K \sqrt{l}$ — the equilibrium kinetic factor involved in the Nicholson and Shain treatment of this mechanism[14]. A simple modification of their approach permitted a ready analysis of the experimental data without recalculation of working curves.

EXPERIMENTAL

The basic instrumentation consisted of a Bioanalytical Systems Inc Cyclic Voltammeter Model CV-1A which incorporates a three-electrode potentiostat, linear potential sweep generator with automatic reverse for cyclic voltammetry, and a current to voltage converter output. This fed to a Bryans 2900 A4 X–Y recorder.

The working electrode consisted of a novel design of stationary mercury electrode. A short piece of wide bore capillary tube was fused to a length of glass tubing. The capillary was filled with clean mercury using a Pasteur pipette. This made electrical contact through a platinum wire fused into the glass contact. In turn, a copper wire contact was fused to the platinum. The effective mercury electrode area was determined by chronoamperometric analysis of a $1 \cdot 10^{-3}$ mol . . dm^{-3} Cd^{2+} solution in $1 \cdot 0$ mol dm^{-3} potassium chloride. Using $D = 7 \cdot 83 \cdot 10^{-6}$ cm^2 s^{-1} for Cd^{2+}, the average area was found to be $3 \cdot 39 \cdot 10^{-2}$ cm^2. The mercury was renewed for each run. This design was found to be more convenient than the traditional hanging mercury drop electrodes. The counter electrode was of platinum gauze and the reference electrode was a saturated calomel electrode. All potentials are therefore given versus the SCE.
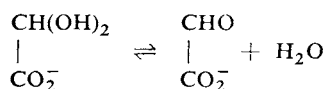
Glyoxylic acid (BDH) was used as received. Most experiments were carried out in a buffer solution made from $0 \cdot 2$ mol dm^{-3} boric acid (BDH Analar) adjusted to pH $9 \cdot 0$ with $0 \cdot 1$ mol . . dm^{-3} tetramethylammonium hydroxide (BDH 25%). For variable pH studies a buffer mixture of $0 \cdot 04$ mol dm^{-3} of each of phosphoric acid, acetic acid and boric acid (all BDH Analar) was adjusted to the required pH with $2 \cdot 0$ mol dm^{-3} sodium hydroxide solution (BDH Analar). All solutions were made up in distilled, deionised water and were deaerated with oxygen free nitrogen.

Experiments were carried out at 20°C (293 K). The experimental data were fitted to the theoretical expression by means of a basic linear least squares program in a Commodore PET minicomputer.

RESULTS AND DISCUSSION

We have studied the voltammetry of a glyoxylate over the pH range $3 \cdot 5$ to $9 \cdot 0$. In this range $dE_p/dpH = 0 \cdot 035 \pm 0 \cdot 01$ V per pH unit. i_k decreased with pH for a given sweep rate (Fig. 1). This shift reflects the increasing proportion of free glyoxylic acid in the reaction mixture (for which $K = 6 \cdot 10^{-4}$) and an increasing amount of acid catalysed dehydration.

At pH $9 \cdot 0$ glyoxylate is reduced at a peak potential of $-1 \cdot 1$ V, less negative than that for oxalic acid, $E_p = -1 \cdot 83$ V. One might expect therefore that the reduction of oxalic acid would proceed directly to a product corresponding to the reduction of glyoxylate (e.g. malate or glycollate). However, under our conditions it does not appear to do so, but stops at the glyoxylate stage. This is presumably due to the relatively slow kinetic step preceding the reduction of glyoxylate, i.e. the dehydration of glyoxylate hydrate.

$$\begin{array}{ccc}
\text{CH(OH)}_2 & & \text{CHO} \\
| & \rightleftharpoons & | \quad + \ \text{H}_2\text{O} \\
\text{CO}_2^- & & \text{CO}_2^-
\end{array}$$

We should therefore expect a kinetically controlled reduction wave, as observed by Kůta[11,12].

Saveant and Vianello[15] have discussed in detail the application of voltammetry to the CE mechanism for reversible electron transfer.

$$Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O \overset{+ne}{\rightleftharpoons} R$$
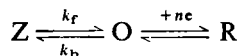
They define a dimensionless kinetic parameter λ, where

$$\lambda = (k_f + k_b)/v \cdot \frac{RT}{nF} \, ,$$

where k_f and k_b are forward and reverse rate constants respectively (unimolecular or pseudounimolecular) and v is the potential sweep rate $(V\ s^{-1})$. They define criteria within which their working curves are applicable. For example, for $K = k_f/k_b < 0.5$ a useful range of λ is $0.025 < \lambda < 100/K^2$. For sweep rates between 0.01 and $500\ V\ s^{-1}$ accessible values of k are given by $0.01\ s^{-1} < k < (2 \cdot 10^6/K^2)\ s^{-1}$.

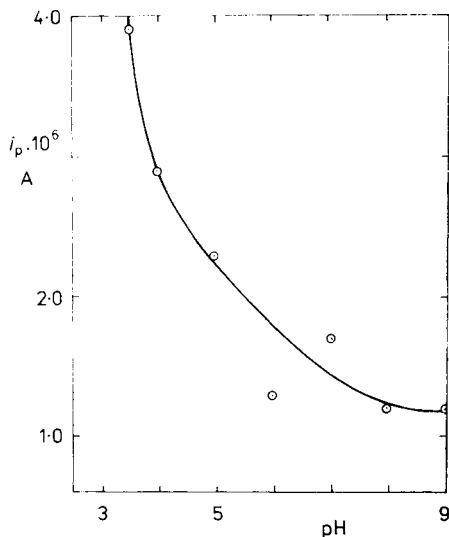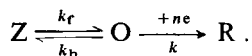Nicholson and Shain[14] treat the same problem for both the reversible case and for the irreversible case,

$$Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O \overset{+ne}{\underset{k}{\longrightarrow}} R \, .$$

FIG. 1

Graph of i_p vs pH for 0.002M glyoxylic acid

They define their kinetic parameter, ψ, slightly differently,

$$\psi_{rev} = \sqrt{a}/K\sqrt{l},$$
$$\psi_{irrev} = \sqrt{b}/K\sqrt{l},$$

where $a = (nF/RT)v$; $b = (\alpha n_a F/RT)v$; $l = k_f + k_b$, i.e. $\psi = K/\sqrt{\lambda}$.
Similar working curves are given for i_k/i_d versus ψ, and for potential versus $\log \psi$, where i_k is the observed kinetic current and i_d is the theoretical diffusion limited peak current.

Nicholson and Shain[14] have also given an empirical expression which fits the former working curve to within at least $\pm 1 \cdot 5\%$, compared with the $\pm 5\%$ accuracy commonly accepted for measurements of i_p. The empirical equation is

$$i_k/i_d = \frac{1}{1 \cdot 02 + 0 \cdot 471 \sqrt{a}/K\sqrt{l}} \text{ (reversible case)} \tag{1a}$$

or

$$i_k/i_d = \frac{1}{1 \cdot 02 + 0 \cdot 531 \sqrt{b}/K\sqrt{l}} \text{ (irreversible case)}. \tag{1b}$$

For the present work, the data indicates that the irreversible case is the appropriate one. We shall therefore confine our further theoretical development to that case, though similar treatment of the reversible case is obvious.

In the reversible case, i_d may be calculated from the expression[14],

$$i_d = \sqrt{\pi}\chi(at)\, nFACD^{1/2}b^{1/2} \tag{2}$$

which with the maximum (peak) value of $\sqrt{\pi}\chi(at) = 0 \cdot 4958$, becomes

$$i_d = 0 \cdot 4958 nFACD^{1/2} \left(\frac{\alpha n_a F}{RT}\right)^{1/2} v^{1/2} = \tag{3}$$

$$= 3 \cdot 01 \, . \, 10^5 n(\alpha n_a)^{1/2} ACD^{1/2} v^{1/2} \text{ at 293 K}.$$

Rearranging Eq. $(1b)$ we obtain,

$$i_d/i_k = 1 \cdot 02 + 0 \cdot 531 \left(\frac{\alpha n_a F}{RT}\right)^{1/2} v^{1/2} \frac{1}{K\sqrt{l}}. \tag{4}$$

A graph of i_d/i_k versus $v^{1/2}$ should give a straight line of slope $0 \cdot 531 \, (\alpha n_a F/RT)^{1/2}$ $(1/K\sqrt{l})$ and intercept $= 1 \cdot 02$, hence giving $K\sqrt{l}$ from which k_f and k_b can be found for a given value of K.

It is not actually necessary to know the value of $\sqrt{\alpha n_a}$ as it is a constant and occurs both in the expression for i_d Eq. (3) on the left hand side of Eq. (4) as well as on the right hand side. Indeed a further rearrangement of Eq. (4) would allow $\sqrt{(\alpha n_a)}$ to be determined from the intercept:

$$\frac{i_d/i_k}{\sqrt{(\alpha n_a)}} = \frac{1\cdot02}{\sqrt{(\alpha n_a)}} + 0\cdot531\,\frac{F}{RT}\,\frac{1}{K\sqrt{l}}\,v^{1/2}\,. \tag{5}$$

The initial data were obtained using $2\,.\,10^{-3}$ mol dm^{-3} glyoxylate. However, the voltammograms were complicated by marked pre-peaks and post-peaks, before and after the main diffusion/kinetic peak Fig. $2a$, b. These are characteristic indications of strong adsorption of both product and reactant respectively[16]. Adsorption does not appear to have been a problem on the DME in Kûta's studies[11,12]. Perhaps he used a surfactant maximum suppressor. We did not. Peak heights were taken from
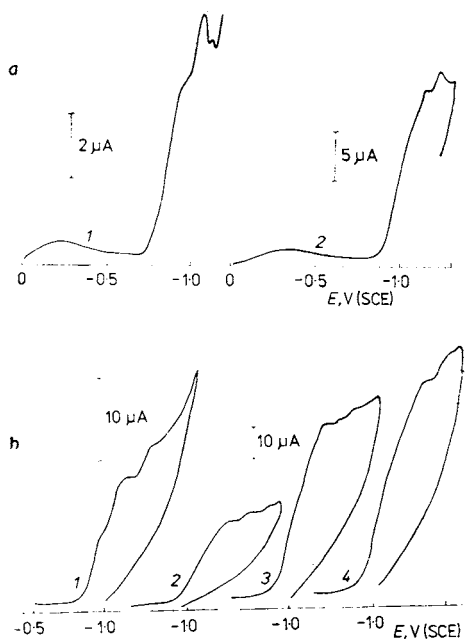

FIG. 2

Voltammograms of 0·002M glyoxylic acid on mercury at pH 9·0. Sweep rate, v (V s^{-1}): a 1 0·02; 2 0·04. b 1 0·1; 2 0·2; 3 0·3; 4 0·4
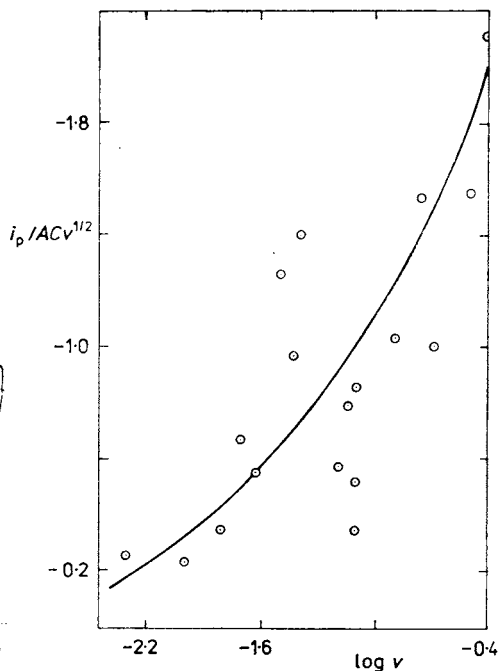
FIG. 3

Graph of $i_p/ACv^{1/2}$ vs log v for 0·002M glyoxylic acid

the middle peak. They were not very reproducible. A graph of current function $(i_p ACv^{1/2})$ against $\log v$ (Fig. 3) shows a marked increase with increasing sweep rate. This is again indicative of strong adsorption[16] overriding the expected decrease for a kinetic wave[14].

TABLE I

Data from voltammetry of $2 \cdot 10^{-3}$M glyoxylate at pH 9·0. $i_d = 3 \cdot 10^5 n(\alpha n_a)^{1/2} ACD^{1/2}v^{1/2} = 6 \cdot 93\, v^{1/2}/10^{-5}$ A, where $n = 2$, $\alpha n_a = 0 \cdot 29$, $A = 3 \cdot 39 \cdot 10^{-2}$ cm^2, $C = 2 \cdot 10^{-6}$ mol cm^{-3}, $D = 1 \cdot 10^{-5}$ cm^2 s^{-1}

$v^{1/2}$	$i_k/10^6$, A	i_d/i_k	$K\sqrt{l}$
0·100	1·42	4·88	0·04
0·122	2·03	4·18	0·07
0·158	7·00	1·56	0·50
0·173	15·13	0·79	−1·27
0·245	5·80	2·93	0·23
0·283	10·90	1·80	0·65
0·316	19·40	1·13	4·45
0·374	31·75	0·82	−3·32
0·447	29·50	1·06	18·77
0·548	57·00	0·67	−2·84
0·632	86·50	0·51	−2·20

TABLE II

Data from voltammetry of $2 \cdot 10^{-1}$M glyoxylate at pH 9·0. $i_d' = 3 \cdot 10^5 n ACD^{1/2}v^{1/2} = 0 \cdot 01286\, v^{1/2}$, where $n = 2$, $A = 3 \cdot 39 \cdot 10^{-2}$ cm^2, $C = 2 \cdot 10^{-4}$ mol cm^{-2}, $D = 1 \cdot 10^{-5}$ cm^2. s^{-1}

v, mV s^{-1}	$v^{1/2}$	$i_k \cdot 10^4$, A	i_d'/i_k
0·030	0·1732	4·28	5·21
0·040	0·200	4·50	5·72
0·060	0·245	4·33	7·29
0·080	0·283	4·58	7·95
0·100	0·316	4·80	8·49
0·120	0·346	4·61	9·68
0·140	0·374	4·50	10·71
0·160	0·400	4·38	11·76
0·180	0·424	4·60	11·88
0·200	0·447	4·93	11·68

The data seldom fitted Eq. ($1b$) except at lower sweep rates where adsorption effects are minimised[16] (Table I). Wopshall and Shain's attempts to separate adsorption and kinetic effects theoretically were not markedly successful. However, their empirical method of extrapolating experimentally observed rate constants to zero sweep rate was much more successful[17]. This technique would not work reliably with our data as many of the $K\sqrt{l}$ values (Table I) were negative owing to i_d/i_k being greater than 1·02, i.e. the adsorption effect outweighs the kinetic effect. Even so, if one takes the positive values of $K\sqrt{l}$ and plots log $K\sqrt{l}$ against v, the intercept at $v = 0$ gives $K\sqrt{l} = 0·04$.

A complementary approach is to increase the reactant concentration to a point where the adsorption contribution is minimal[16]. The concentration of glyoxylate was increased one hundred fold to 0·2 mol dm^{-3}. Calculation of $K\sqrt{l}$ values for a range of sweep rates using Eq. ($1b$) (Table II) gave acceptable values. A graph of i_d/i_k versus $v^{1/2}$ (Eq. (4)) gave a straight line. The data for this graph were analysed by a linear least squares computer program to give the following parameters: Correlation coefficient 0·992; slope 24·7 $\pm$ 0·4; intercept 0·983 $\pm$ 0·059. At pH 9·0, $K\sqrt{l}$ was 0·135 $\pm$ 0·002.

Using Kůta's value of $K = 0·016$ (no error given)[12], one can calculate that $k_f = 1·14 \pm 0·03$ s^{-1} and $k_b = 70 \pm 2$ s^{-1}. The value determined by Ahrens[13] using temperature jump methods would be totally dominated by the base catalysed reaction at pH 9, giving $k_f = 2·6 \pm 2·0$ s^{-1}. From this and Ahrens value for $K = 0·0606 \pm 0·0092$ (determined spectroscopically), $k_b = 42·9 \pm 33·6$ and hence $K\sqrt{l} = 0·41 \pm 0·16$. The accuracy of our value of k_b would appear to be much greater than that of Ahrens[13]. However, any comparison is complicated by the large discrepancy between the values for K of Ahrens[13] and Kůta[12].

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