SHORT COMMUNICATION

Electro-oxidative Decarboxylation of D-Gluconic Acid to D-Arabinose on Graphite Electrodes

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ABSTRACT

A voltammetric investigation of the direct electro-oxidative decarboxylation of D-gluconate ion to D-arabinose on spectroscopic graphite electrode from methanol–water mixtures as well as from aqueous solutions is described. Practically a 100% yield in D-arabinose and an 80% yield in current were realized. The kinetic behavior points to a rate-determining release of the first transferring electron from the gluconate anion to the electrode, followed by a cleavage of the C-1–C-2 bond and by the resulting decarboxylation.

KEY WORDS: D-Gluconic acid, oxidation, graphite electrode, decarboxylation

INTRODUCTION

The electro-oxidative decarboxylation of D-gluconic acid, D-glucono-lactone, or glucose to D-arabinose is of commercial relevance, and has been extensively studied during the last decade [1–9]. This electrochemical oxidation has been commonly carried out indirectly, using cerium sulfate as a mediator, although direct electro-oxidation of D-gluconic acid to D-glucose on graphite [7] has been reported. In addition, Smith *et al.* [9] have investigated the direct electro-oxidation of levoglucosan to D-arabinose on a glassy carbon electrode by cyclic voltammetry.

This communication reports a voltammetric investigation of the direct electro-oxidative decarboxylation of D-gluconate ion to D-arabinose on carbon electrodes from methanol–water mixtures as well as from aqueous solutions. Several types of carbon electrodes prepared according to Partiarche and co-workers [10] were employed, but only spectroscopic graphite turned out to yield satisfactory results.

EXPERIMENTAL

All reagents, including methanol, were either Merck or Fluka analytical reagent grade, and were used without further purification. Solutions were prepared from distilled water treated by the Milli-Q water system. Rods of spectroscopic graphite were supplied by Le Carbon-Lorraine (France); the same graphite was also used as the electrode material for the rotating disk electrode. All graphite rods were impregnated with paraffin. To this end they were immersed in fused paraffin in a thick-walled test tube, kept under vacuum for 10 min, and finally brought back to atmospheric pressure to fill the pores with paraffin. The working surfaces were ground with ultrafine emery paper before use.

Voltammetric measurements were carried out with an AMEL 473 polarographic three-electrode system, using a Metrohm 628-10 rotating disk electrode. An aqueous S.C.E. served as the reference electrode and a platinum wire as the auxiliary electrode. All pH measurements, including those in methanol–water mixtures, were carried out with a Metrohm 6.0102.000 glass electrode, which was calibrated against two standard aqueous buffers. Therefore, the pH values reported for the methanol–water mixtures are only formal values, which do not provide a direct measure of hydroxonium activity in these mixtures.

Controlled-potential electrolyses were carried out in an H-shaped cell divided by a medium-porosity glass sinter. The anode consisted of two graphite rods in contact both with each other and with a few graphite rod fragments lying on the bottom of the anodic compartment; the analyte, 10 cm^3 in volume, was stirred by a teflon helical stirrer mounted in place of the rotating disk electrode. The counter-electrode in the cathodic compartment was a platinum foil. Analysis of the analyte was carried out by HPLC [Polispher OA-KC column (300 × 7.8 mm) together with a Perkin Elmer LC Analyst].
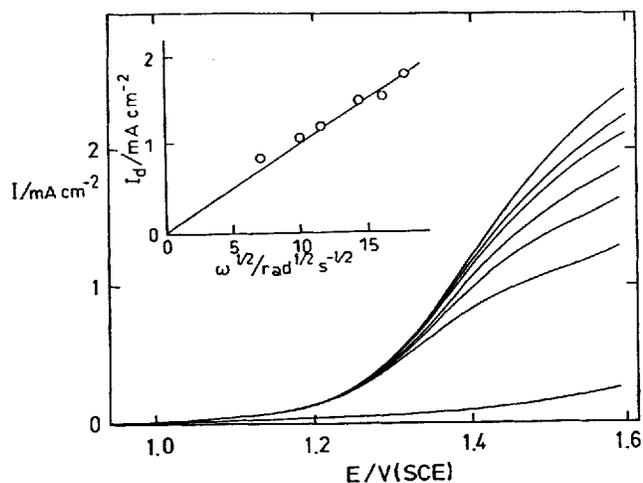

In memory of Professor Gaston Patriarche.
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RESULTS AND DISCUSSION

Attempts to carry out electrolysis on a glassy carbon electrode were unsuccessful. Upon subjecting a solution of 5 × 10^{-3} M sodium gluconate (GL), in an unbuffered 90% (v/v) methanol–water mixture containing 0.2 M tetrabutyl-ammonium (TBA) perchlorate, to a positive potential scan on a freshly polished glassy carbon rotating disk electrode (RDE), an anodic voltammetric curve was obtained with a half-wave potential of about + 1.39 V/SCE. However, the recording is accompanied with the deposition of a brownish insoluble product that inhibits the electrode process. Thus, upon holding the applied potential at a constant value along the rising portion of the plateau of the voltammogram, the current decreases rapidly and ultimately vanishes. Analogously, no anodic voltammogram is observed when reversing the potential scan after having recorded the whole anodic voltammogram in the positive direction. The brownish deposit is partly electroreduced upon scanning the applied potential in the negative direction up to ca − 2.0 V; in this case, a further recording in the positive direction yields once again the anodic voltammogram, although its height decreases progressively as this operation is repeated. No attempt was made to determine the nature of the insoluble product.

As opposed to glassy carbon, spectroscopic graphite does not lead to insoluble products under the same experimental conditions. Conversely, after repeating potential cycling from + 0.8 to + 1.6 V, stable voltammograms are obtained, even though the backward voltammogram is slightly shifted in the positive direction with respect to the forward one. The magnitude of this hysteresis decreases progressively on decreasing the scan rate, being quite small at scan rates ≤ mV/s. All voltammograms reported

were recorded in the forward direction at a scan rate of 5 mV/s.

Figure 1 shows a number of voltammograms of 5 × 10^{-3} M NaGL in 90% (v/v) methanol–water containing 0.2 M TBAClO$_4$ as recorded at different rotation rates, ω, together with the voltammogram of the supporting electrolyte alone (namely, the residual current vs. E), as recorded at the lowest rotation rate. The inset shows a plot of the limiting current, i_ℓ, as measured from the residual current recorded at the same rotation rate, against $\omega^{1/2}$. The half-wave potential, $E_{1/2}$, is about + 1.325 V. The plot is linear and passes through the origin, in agreement with the Levich equation for a diffusion-controlled limiting current. Over the accessible concentration range of NaGL in this medium (namely from the minimum detectable concentration of 1 × 10^{-3} M up to 1 × 10^{-2} M) the height of the anodic voltammogram of GL is proportional to GL concentration. This voltammogram yields a linear plot of $\ln[i/(i - i)]$ vs. FE/RT, where i is the faradaic current at the applied potential E as measured upon correcting the experimental current for the corresponding residual current. The slope of this plot, which measures the charge transfer coefficient α, equals 0.45.

Attempts were made to buffer the solutions of NaGL + 0.2 M TBAClO$_4$ in 90% (v/v) methanol–water by additions of formate, acetate, phosphate, carbonate, or borate buffers. Satisfactory stable and reproducible voltammograms were obtained only with the acetate buffer. The shape and half-wave potential of the anodic voltammogram of GL is independent of the acetate buffer composition and practically coincides with that obtained in the absence of buffers. Figure 2 shows plots of $E_{1/2}$ vs. the formal pH both in the presence of acetic acid and at different acetate buffer compositions; the horizontal straight line denotes the $E_{1/2}$ value as obtained in the

FIGURE 1. Current density vs. potential curves for 5 × 10^{-3} M NaGL electro-oxidation from 90% methanol containing 0.2 M TBAClO$_4$, as recorded (from the bottom upwards) at rotation rates of 500, 1000, 1500, 2000, 2500, and 3000 revolutions per minute (the lowest voltammogram was obtained in the absence of NaGL at a rotation rate of 500 revolutions per minute). The insert shows the corresponding plot of the diffusion limiting current I_d vs $\omega^{1/2}$.
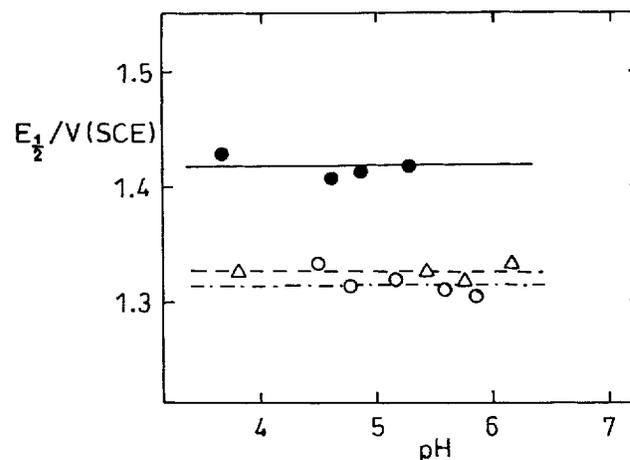
FIGURE 2. $E_{1/2}$ vs. pH plots for 5 × 10^{-3} M NaGL electro-oxidation from 0.1 M acetate buffers in 90% methanol (△), 50% methanol (○), and pure water (●). The horizontal straight lines mark the $E_{1/2}$ values obtained from unbuffered solutions of 0.1 M CH$_3$COONa in 90% methanol (————), 50% methanol (—·—·—·—·—), and pure water (————).

absence of buffers. We may therefore conclude that the kinetics of GL electro-oxidation in the present medium is independent of pH.

The nature of the electrolysis product, as well as the product and current yields, were estimated by carrying out controlled-potential macroelectrolysis as described in the experimental part. The starting solution consisted of 1 × 10^{-2} M NaGL + 0.2 M TBAClO$_4$ in 90% (v/v) methanol–water and was electrolyzed at +1.30 V, where the residual current was initially 9% of the whole current. Naturally, during electrolysis at constant potential, the whole current decreases toward the residual current; the latter remains nearly constant during electrolysis, as ascertained by independent measurements carried out in the absence of NaGL under otherwise identical conditions. The macroelectrolysis was repeatedly interrupted to permit the recording of the anodic voltammogram resulting from GL electro-oxidation on a freshly polished graphite rotating disk electrode, and thus the GL concentration was being monitored in the anodic compartment of the electrolysis cell. The charge that passed before each voltammetric measurement of GL concentration was obtained by graphical integration of the current flowing through the electrolysis cell during the macroelectrolysis. Upon plotting this charge, suitably corrected for the contribution from the residual current, against the corresponding decrease in the number of GL moles, a straight line is obtained; the slope of this line indicates that GL electro-oxidation consumes two Faradays per mole. This result is confirmed by a series of macroelectrolyses that were interrupted after the flow of different amounts of charge and followed by a quantitative analysis of the partially electrolyzed solutions by HPLC. Comparison with authentic samples revealed the presence of D-arabinose; moreover, the sum of the number of moles of unreacted GL and of D-arabinose was found to be constantly equal to the number of moles of GL in the starting solution, within the limits of experimental error. In addition, the number of moles of D-arabinose in any of the partially electrolyzed mixtures was found to be one half of the number of Faradays employed in the corresponding macroelectrolysis, provided the latter number was corrected for the contribution from the residual current. Therefore, the yield in D-arabinose was practically 100%. The yield in current depends upon the potential selected for the macroelectrolysis. In fact, a negative shift in this potential increases the ratio of the faradaic to the residucal current and hence the current yield, but at the same time increases the duration of the electrolysis. Under the present experimental conditions, the current yield is about 75%.

A gradual increase of water content in the methanol–water mixture causes oxygen discharge to approach the rising portion of the GL oxidation curve, thus reducing the length of its plateau and ultimately obliterating it. This is apparent from Figure 3, which shows the voltammograms of a buffered 50% (v/v) methanol–water mixture and of a buffered aqueous solution, both in the absence and in the presence of 5 × 10^{-3} M NaGL. Here too, satisfactorily reproducible voltammograms were obtained in the presence of acetate buffers. Even though the voltam-

mograms of Figure 3 in the presence of GL do not show any plateau, distinct waves are obtained upon subtracting from these voltammograms the corresponding voltammograms in the absence of GL (see the dashed curves in Figure 3). The latter waves permitted us to estimate the half-wave potential $E_{1/2}$ as a function of pH both in 5% (v/v) methanol–water mixtures and in aqueous solutions, over the pH range covered by acetate buffers of different composition. Figure 2 shows that $E_{1/2}$ is independent of pH from 90% (v/v) methanol–water mixtures up to pure water. Moreover, the GL wave obtained from an unbuffered solution of sodium acetate practically coincides with those obtained from acetate buffers of different compositions for all investigated methanol–water mixtures. The quantity $(E_{3/4}-E_{1/4})$ relative to GL waves obtained as shown in Figure 3 takes values close to 0.1 V, where $E_{1/4}$ and $E_{3/4}$ are the potentials at which the faradaic current i equals 1/4 and 3/4 of its diffusion limiting value, respectively. Noting that for an irreversible wave this quantity equals 0.056 α, we may conclude that the charge transfer coefficient α lies in the proximity of 0.5 for all methanol–water mixtures investigated. Macroelectrolyes of 1 × 10^{-2} M NaGL from buffered 50% (v/v) methanol–water mixtures and of 0.1 M NaGL from buffered aqueous solutions were carried out by the same procedure described for the 90% (v/v) methanol–water mixtures, and were likewise followed by a

FIGURE 3. Current vs. potential curves obtained from 0.1 M CH$_3$COONa in 50% methanol both in the absence and in the presence of 3 × 10^{-3} M NaGL (a) and from 0.1 M CH$_3$COONa in pure water both in the absence and in the presence of 5 × 10^{-3} M NaGL (b); the dashed curves were obtained upon subtracting the residual current from the corresponding current in the presence of NaGL.
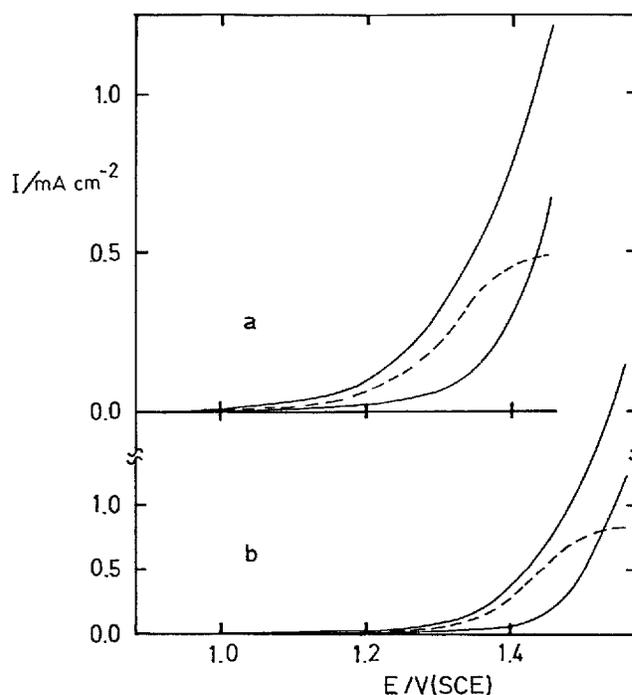
HPLC analysis. In both solvents, the yield in D-arabinose was found to be practically 100%.

The above experimental findings lend themselves to the following mechanistic conclusions. For an electrode process consisting of a sequence of electrochemical and chemical steps, the charge-transfer coefficient α equals ($\tilde{n}$ + β) if the rate-determining step (rds) is electrochemical and $\tilde{n}$ if it is chemical; here $\tilde{n}$ is the number of electrons transferred prior to the rds and β is the symmetry factor of the electrochemical rds. Taking into account that β has values that are usually close to 0.5, the α value for GL electro-oxidation points to an electrochemical rds involving the release of the first transferring electron to the electrode material ($\alpha = \beta \approx 0.5, \tilde{n} = 0$). Moreover, the pH independence of the electrode kinetics indicates that the electrochemical rds is not preceded by chemical deprotonation steps. Even though there is no way of elucidating the nature of the elementary steps following the rds, it is quite plausible to postulate that the release of the first transferring electron by the GL anion to the electrode leads to a cleavage of the C-1–C-2 bond and to the resulting decarboxylation. The release of a second electron by the resulting neutral radical would then be followed by the release of a proton, yielding the final product, D-arabinose.

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