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THE ELECTROREDUCTION OF CO_2 TO GLYCOLLATE ON A LEAD CATHODE

A. Bewick and G.P. Greener

Department of Chemistry, University of Southampton, England.

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We reported recently[1] the synthesis of malate by the electroreduction of carbon dioxide on a mercury cathode. The extension of this work to include the use of other high hydrogen-overvoltage cathodes has produced other interesting syntheses.

Carbon dioxide was successfully reduced at a lead cathode in aqueous solutions of quaternary ammonium salts, a carbonate/bicarbonate buffer being used to maintain the pH at 8.3. A number of cathodic potentials were employed in the range -1.5v to -2.2v (vs. N.H.E.) and the electrode potential was controlled with a potentiostat. A divided cell was used with the anode and cathode compartments separated by a cationic exchange membrane (Permaplex C20). A single product was obtained over the whole range of potential. The methods used for qualitative analysis were basically similar to those previously described[1]. Figure 1 shows infra red spectra from a cell sample and from a standard sample of tetramethylammonium glycollate. The absence of formate in the product is surprising in view of the facts that we have obtained up to 30% coulomb yield of this on a mercury cathode under similar conditions, and that the hydrogen evolution reaction is very much faster on lead, Figure 2.

The glycollic acid was quantitatively analysed by degrading it to formaldehyde using concentrated sulphuric acid. The amount of formaldehyde obtained was determined by complexing with chromotropic acid and measuring the optical density of the solution at 570 mμ[2]. The yield-potential curve is shown in Figure 3. The yield curve shows a pronounced minimum similar to that obtained for the synthesis of malate on mercury. The lower yields at higher potentials are due to the greater importance of the hydrogen evolution reaction on lead, most of the current at high potentials being due to this reaction (see Fig. 2).

If allowance is made for this parallel reaction, the yield curves for the two hydroxy acids are remarkably similar. It is interesting to note that glycollic acid and malic acid are related by a dimerisation with elimination of water.

The coulomb yields are greatly in excess of 100% at a number of potentials and this was also the case for malate synthesis. Again, therefore, the reduction must follow a combined chemical and electrochemical mechanism and the brief discussion given in the earlier paper applies to the present case.

Additional kinetic information on the details of the electrochemical steps was obtained using conventional, non-steady state electrochemical techniques and will be presented elsewhere. Part of this information is directly relevant to the present discussion. Current-time transients were obtained by stepping the potential cathodically into a region where the reaction rate becomes limited by the diffusion of carbon dioxide molecules to the electrode surface. Analysis of these transients showed that only one electron was required for every two molecules of carbon dioxide used in the overall reduction to glycollate. This is exactly the ratio required to explain the 600% coulomb yield calculated from the results of chemical analysis and thus two completely independent calculations confirm this important conclusion. Corroborative evidence of the same kind is also available for the synthesis on mercury cathodes for which the chemical analysis gave coulomb yields of malate up to 800%.

References

1. A. Bewick and G.P. Greener, Tetrahedron Letters 1969. In Press.
2. C.E. Bricker and H.R. Johnson, Ind. Eng. Chem., 17, 400 (1945).

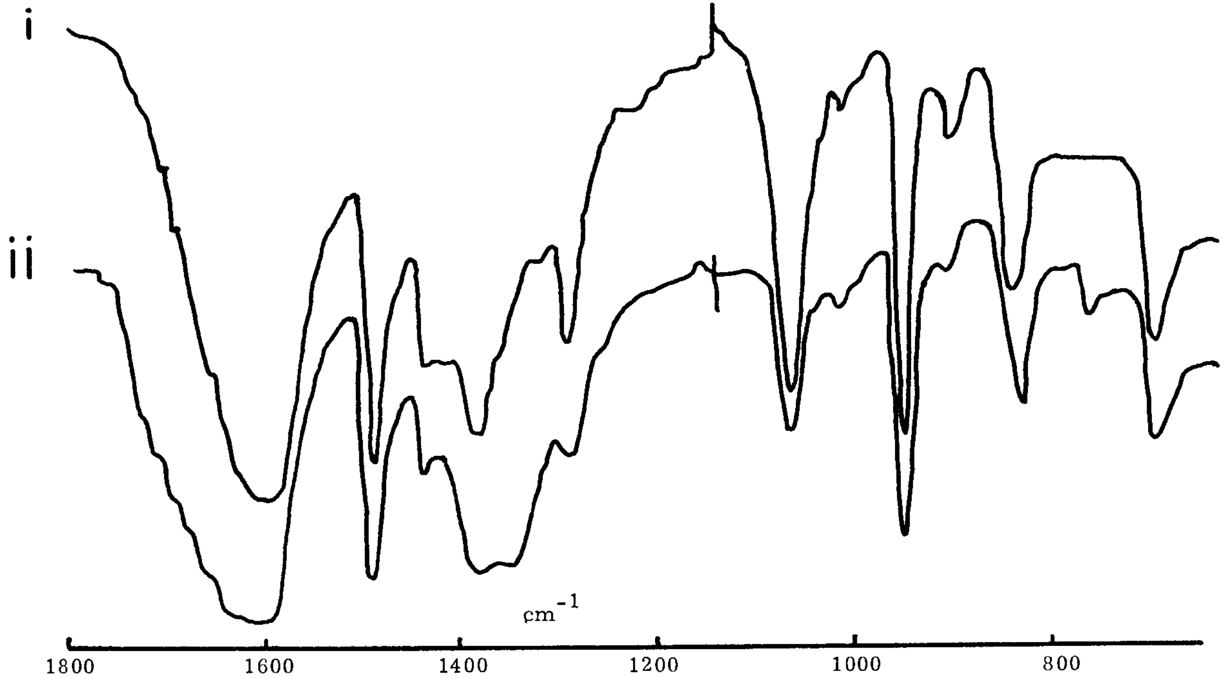
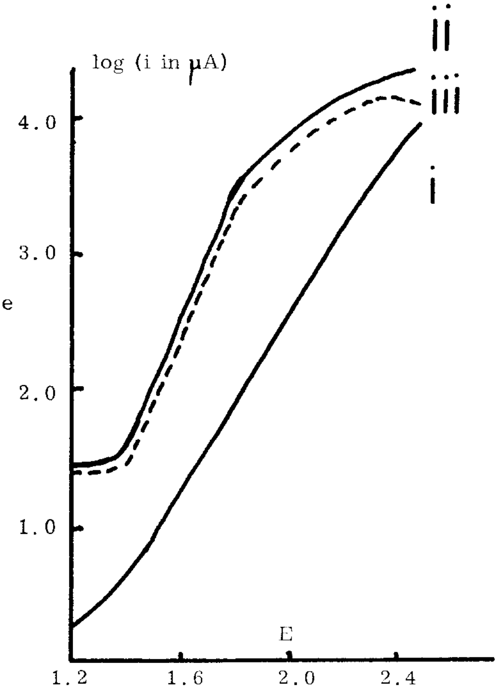


Figure 1

(i) I.R. spectrum of tetramethylammonium glycollate standard.

(ii) I.R. spectrum of dried cell sample.



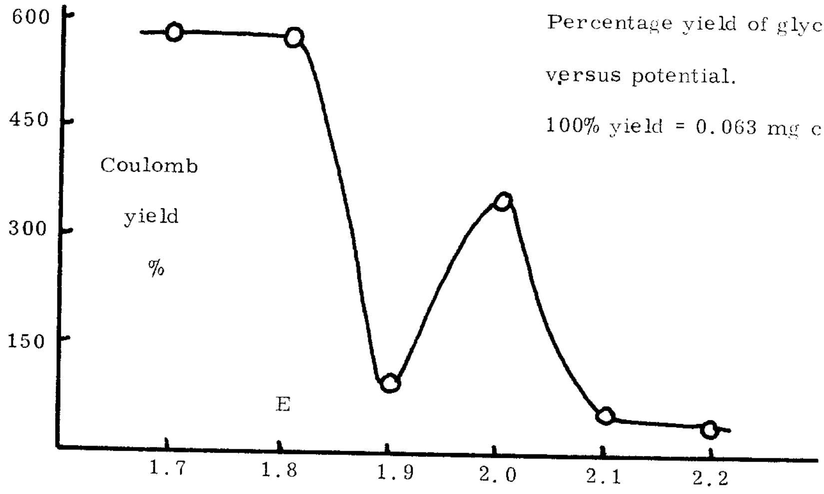
Polarisation curve for the reduction of CO_2 on Pb (electrode area 0.6 cm^2)

(i) Background current

(ii) Total current

(iii) Curve (ii) minus curve (i)

Figure 2



Percentage yield of glycollic acid versus potential.

100% yield = 0.063 mg $coulomb^{-1}$.

Figure 3