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THE ELECTROREDUCTION OF CO_2 TO MALATE ON A MERCURY CATHODE

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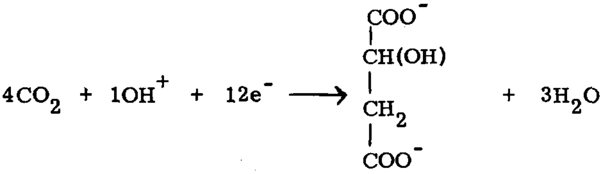
Carbon dioxide and water are ideal feedstocks for organic synthesis. We wish to report the discovery of a novel process for the fixing of carbon dioxide with the production of more complex molecules.

Carbon dioxide was reduced electrochemically at controlled potential on a mercury cathode in aqueous solutions of quaternary ammonium salts. An irreversible cathodic process begins at about -1.4 volts (vs. N.H.E.) and can be followed out to about -2.6 volts. The products obtained from steady state electrolyses at a number of potentials were analysed and found to be malate together with a smaller amount of formate. Formate was expected (1) and identified by chemical tests but infra red spectroscopy indicated the presence of another carboxylate species. Further chemical tests on the catholyte after removal of formate gave a positive indication for both an α and a β hydroxy acid. Accordingly, any free acid was liberated from the catholyte using an ion exchange column (Amberlite I.R.120). The elluent was freeze dried and run on paper with a butanol/acetic acid/water solvent. A single, well defined acid spot was obtained corresponding exactly in position to a malic acid standard. Paper chromatography on the untreated catholyte gave the same result. The infra red spectrum of material from a preparative chromatogram was compared with that from pure malic acid and found to be identical.

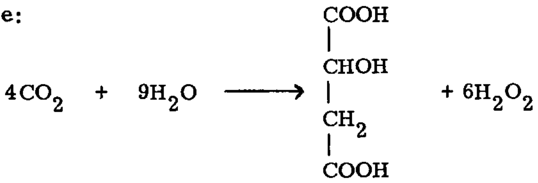
The malate was analysed quantitatively by a colourimetric method. The total amount of malate in a sample was complexed with Mo(IV). The excess Mo(IV) present was reduced with chlorostannous acid and the resulting blue Mo(III) was estimated spectrophotometrically at 725 mμ. The procedure was checked with malate standards.

The stoichiometric equation for a full electrochemical reduction of CO_2 to malic acid is



$$4CO_2 + 10H^+ + 12e^- \longrightarrow \begin{array}{c} COO^- \\ | \\ CH(OH) \\ | \\ CH_2 \\ | \\ COO^- \end{array} + 3H_2O \qquad (1)$$

In most cases we have found that the amount of malate produced corresponds, on the basis of equation (1), to a coulombic yield greatly in excess of 100%. The yield-potential curve is shown in figure 1. This implies that the reaction cannot be purely electrochemical in nature. The question arises as to what the reaction can be. The possibility of hydrogen abstraction from the quaternary ammonium salt was investigated by looking for amines in the product by means of G. L. C. and by quantitatively analysing the quaternary ammonium ion before and after constant potential electrolysis by means of its complex with ammonium reineckate (2). No amines were detected and the quantitative analysis showed that quaternary ammonium ions were not consumed. The only remaining possibility is reduction via the water molecules and, as an example, the following equation would illustrate the reduction process if it took place by a completely chemical route:



$$4CO_2 + 9H_2O \longrightarrow \begin{array}{c} COOH \\ | \\ CHOH \\ | \\ CH_2 \\ | \\ COOH \end{array} + 6H_2O_2 \qquad (2)$$

Clearly reactions (1) and (2) can be combined in suitable ratios to give any desired coulombic yield greater than 100%. We felt reluctant at first to postulate reaction (2) as a possibility. Although we satisfied ourselves that there was enough free energy available to drive this reaction we expected that hydrogen peroxide would be reduced at the potentials at which we were operating. The high coulombic yields observed would only be obtained if the hydrogen peroxide was not reduced. Accordingly, we investigated the electrochemical reduction of hydrogen peroxide under our experimental conditions. The reduction was found to be very slow and verified that hydrogen peroxide or an equivalent species could be involved in the reduction of carbon dioxide.

The novel combined chemical and electrochemical mechanism that we have suggested has a number of interesting features. From our results it follows that it is possible to synthesise malic acid with the consumption of only $^3/8$ of an electron per molecule of carbon dioxide. There must be, therefore, a chain electron transfer mechanism in which a single electron can successively activate several molecules. We envisage that an adsorbed layer of tetraalkylammonium cations provides an essentially non-aqueous environment where this sort of reaction might take place. The intermediates involved in the process are a matter of conjecture. Presumably a CO_2 molecule receives an electron to form an anion radical. The mediation of the adsorbed layer may well cause such intermediates to react with more CO_2 molecules. The size of the transition state which may be achieved could be determined by the properties of the adsorbed layer which would also determine the relative orientation and availability of water molecules allowing the resulting hydrogen abstraction process. This specific action of the adsorbed layer could be compared with the properties of ion exchange membranes or enzymes.

The synthesis is not only of interest as a means of making a useful material from readily available and inexpensive starting materials with the consumption of a relatively small amount of electric power but has far reaching implications if an analogy with the photosynthetic fixation of CO_2 is sought. We are, at present, seeking to modify the highly specific conditions on the electrode surface in order to achieve different results.

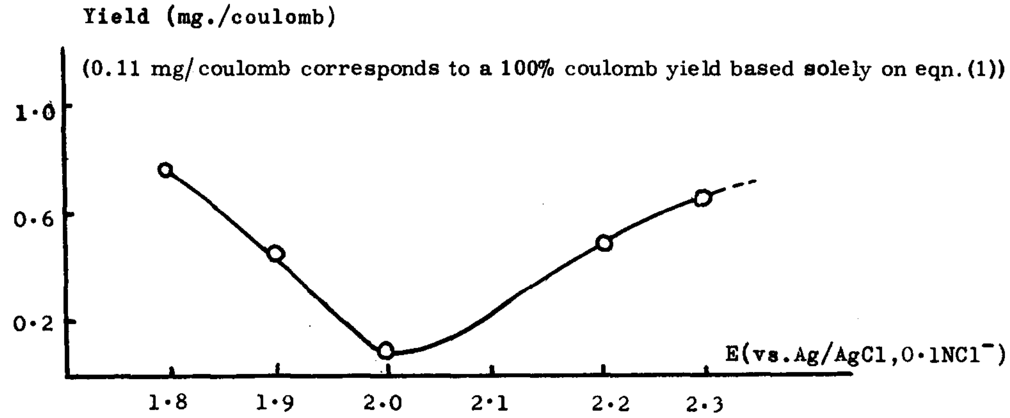


Figure 1. Yield of Malic Acid as a Function of Potential

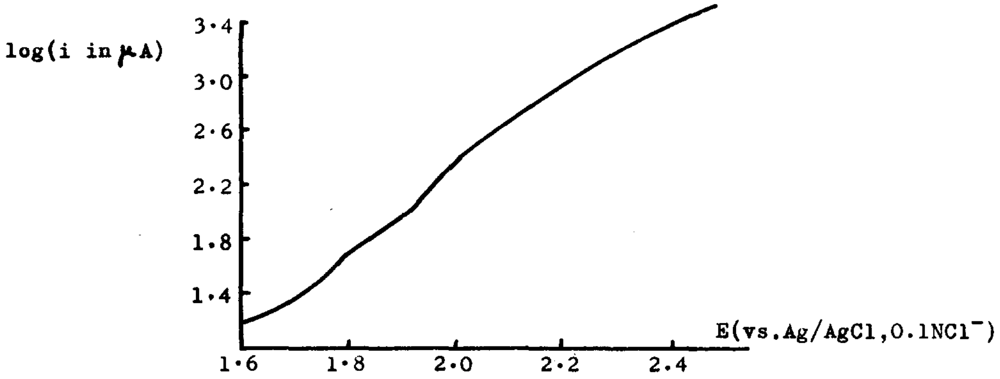


Figure 2. Current - Potential Curves for the Reduction of CO_2 on a Mercury Cathode (Electrode Area 0·06sq.cm.)

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