JOURNAL OF APPLIED ELECTROCHEMISTRY **20** (1990) 54-59

A microelectrode study of the reduction of formaldehyde in neutral concentrated aqueous solutions

M. I. MONTENEGRO

Centro de Quimica Pura e Aplicada da Universidade do Minho, Largo do Paco, 4719 Braga Codex, Portugal

D. PLETCHER

Department of Chemistry, The University, Southampton SO9 5NH, UK

E. A. LIOLIOS, D. J. MAZUR, C. ZAWODZINSKI

The Electrosynthesis Co. Inc., PO Box 430, East Amherst, New York 14051, USA

Received 13 March 1989

Voltammetry at Hg microelectrodes has been used to investigate the mechanism of the reduction of formaldehyde in conditions close to those employed for the electrosynthesis of ethylene glycol (that is, a very high concentration of formaldehyde in a neutral buffer at high temperature). It is shown that, even with a 40% formaldehyde solution, it is possible to record a well formed reduction wave, limiting current densities up to $30\,\mathrm{A\,cm^{-2}}$. The variations in half-wave potential, limiting current density and wave shape with formaldehyde concentration are reported and the influence of pH, temperature and electrolyte are considered. With increasing formaldehyde concentration, the transition from $2e^-$ reduction to $1e^-$ reduction is clearly observed. The results led to a re-examination of the influence of cathode material on the yield of ethylene glycol and it is confirmed that graphite is definitely the best choice.

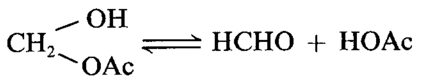
1. Introduction

The mechanism of the reduction of formaldehyde in aqueous solutions has been widely studied by polarography and related techniques [1-12], because the dehydration of formalin is the classical example of a preceding chemical reaction determining the rate of a reduction. Hence in solutions of formaldehyde below $0.6\,\mathrm{mol\,dm^{-3}}$, it has been definitively demonstrated that the cathodic reduction occurs by the mechanism

$$CH_2(OH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCHO + H_2O \qquad (1)$$

$$HCHO + 2H^+ + 2e^- \xrightarrow{\text{fast}} CH_3OH \qquad (2)$$

where the dehydration reaction is the rate determining step. At room temperature the equilibrium constant, K_1, for Reaction 1 has been reported [6] to be 4.4×10^{-4} and the rate constant for the dehydration step, k_1, estimated as $3.4 \times 10^{-2}\,\mathrm{s^{-1}}$ [1, 3, 4]. In fact, commercial formalin contains methanol as a stabiliser and in such solutions free formaldehyde is also in equilibrium with the methanol hemiacetal. The early papers also recognized that buffer components catalysed the hydration and dehydration reactions and Los *et al.* [11] proposed that it was necessary to consider additional equilibria, for example



$$CH_2\!\begin{smallmatrix}OH\\OAc\end{smallmatrix} \rightleftharpoons HCHO + HOAc \qquad (3)$$

in acetate buffer. Then the chemistry of the solutions could be interpreted in terms of equilibrium and rate constants given by

$$10^4\,K_1 = 6.3 + 20.2\,[HOAc] \qquad (4)$$

and

$$k_{-1} = 11 + 53\,[HOAc] + 39\,[OAc^-] \qquad (5)$$

respectively. A complete description of the physical chemistry of the formaldehyde solutions also needs to take into account the dimerisation

$$2\,CH_2(OH)_2 \rightleftharpoons HOCH_2OCH_2OH + H_2O \qquad (6)$$

with an equilibrium constant of 4.5 at room temperature. These polarographic investigations further concluded that the mechanism of reduction changed with pH and different mechanisms taking into account protonation equilibria were proposed [6] for the ranges < 3, 3 to 9 and > 9.

All these studies employed conditions where the formaldehyde reduction led to the formation of only methanol. Recently, however, there has been considerable interest in the hydrodimerisation of formaldehyde to ethylene glycol. This reaction was first reported by Tomilov *et al.* [13, 14] who obtained a 46% organic yield and 25% current efficiency at a graphite cathode in an acidic phosphate buffer. Later a Japanese group [15, 16] reported a higher current efficiency, 83%, using an alkaline solution at 323 K. Since these reports, the Electrosynthesis Co. has developed a very efficient process [17-19]. The recommended process conditions include a low methanol content formate electrolyte,

0021-891X/90 $03.00 + .12

pH 5 to 7, containing a tetraalkylammonium salt, a high formaldehyde concentration (40%), a high temperature (e.g. 363 K) and a cathode chosen from a range of carbons.

The development of microelectrode techniques permits the study of electrosynthetic processes using conditions (e.g. high concentrations of substrate) close to those used in practice [20]. Hence, in this paper, we have set out to use microelectrode techniques to investigate formaldehyde reduction in conditions as close as possible to the process developed by the Electrosynthesis Company. But since it was not possible to construct microelectrodes from carbons known to be similar to those used in the electrosynthesis, most experiments used a Hg microelectrode. In fact, however, the data obtained suggested that Hg is a good choice of cathode for the electrosynthesis and this prompted a re-examination of the choice of cathode; further preparative scale electrolyses were carried out and the results are also reported here.

2. Experimental

The microelectrode experiments were carried out in a two-electrode cell. The working electrode was a 10 μm gold disc plated with mercury. The mercury plating was carried out in acidic, 5 mmol dm^{-3} mercurous nitrate using a diffusion controlled current density for 3 min and the surface was then polished lightly. The surface was replated with Hg every few experiments. The second electrode was an aqueous SCE (Radiometer, type K601).

A Hi-Tek waveform generator, type PPR1, was used directly as the potential source and the cell current was amplified using a current follower based on an RS 071 operational amplifier. The cell and the current follower were placed in a small Al box (Faraday cage); short leads and gold contacts were used between the cell and amplifier. The I–E curves were recorded on a Philips x–y recorder, type PM 8043. All solutions were prepared with analytical grade chemicals and triply distilled water and were degassed with a fast stream of N_2 prior to experiments.

Except where otherwise stated, the electrosyntheses were carried out at 353 K in a MP parallel plate flow cell (ElectroCell AB) with a Nafion type 324 cation exchange membrane. The catholyte was 40% formaldehyde in 1 mol dm^{-3} sodium formate, generally with 1% $(C_4H_9)_4N^+$. The anolyte was 1 mol dm^{-3} sulphuric acid and the anode was lead. With a mercury cathode the electrolyses were carried out in glass cells stirred with a magnetic bar. Both a standard H-cell with a cation membrane separator and a cell designed so that a Hg pool cathode was parallel to a glass frit separator and the counter electrode were used; the results were similar. In addition, data obtained with glass cells and the other cathodes were found to be close to that obtained from MP cell experiments. Current yields of ethylene glycol were determined by gas chromatography after the passage of a charge equivalent to a 20 to 50% conversion of the formaldehyde initially present.

3. Results

3.1. *Microelectrode experiments*

Figure 1 shows a series of i–E curves recorded at room temperature for various concentrations of formaldehyde between 0.04 and 40%. The solutions were pH 7.0 and also contained 1 mol dm^{-3} sodium formate, while the working electrode was a mercury electroplated gold disc radius 5 μm. Also shown are the i–E curves for the electrolyte without formaldehyde. Over the whole range of formaldehyde concentration, a well formed reduction wave is observed at a potential where there is no interference from the reduction of water or electrolyte. The shapes of the waves were analysed by plotting log $((I_L - I)I)$ against E and the slopes of these plots together with the half-wave potentials and limiting current densities are reported in Table 1. Note that the limiting current densities are always low compared with the diffusion limited current density estimated from the equation

$$I_D = i_D/A = 4nFDc/\pi r \qquad (7)$$

where D is the diffusion coefficient (estimated as 5×10^{-6} cm^2 s^{-1}), c the bulk concentration of formaldehyde (including formalin etc.), and r the radius of the microdisc electrode. Indeed the limiting currents for the lowest and highest concentrations of formaldehyde are only approximately 9% and 4% of the calculated

Table 1. Data from I–E curves for the reduction of formaldehyde in 1 mol dm^{-3} aqueous sodium formate, pH 7

Total HCHO conc. (%)	*$-E/V$ w.r.t. SCE*	*$dE/d\log[(I_L - I)/I]$ (mV)*	*I_L (mA cm^{-2})*	*I_L/c (A cm mol^{-1})*
0.04	1.54	95	1.5	112
0.4	1.63	100	18	140
4	1.77	147	270	154
10	1.78	133	460	139
15	1.81	150	640	128
20	1.79	172	710	107
25	1.78	153	650	78
30	1.78	155	570	58
40	1.77	155	620	47

Hg plated Au microdisc electrode, diameter 10 μm. Room temperature.

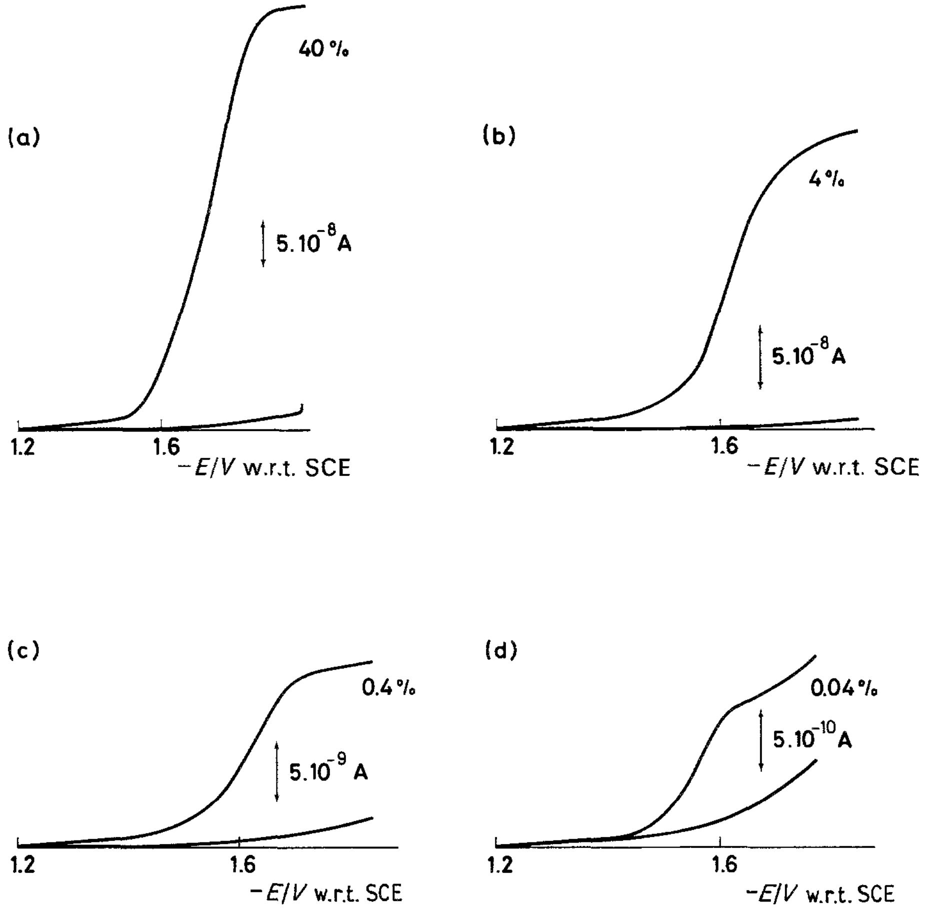


Fig. 1. I–E curves at Hg plated Au microdisc electrode (diameter 10 μm) for the reduction of formaldehyde in 1 mol dm^{-3} sodium formate, pH 7. Room temperature. Potential scan rate 50 mV s^{-1}. Variation of formaldehyde concentration from 0.04 to 40%.

diffusion limited currents, respectively. Clearly, the reduction of formaldehyde is always kinetically controlled largely because of the slow dehydration of formalin, while a decrease in I_L/I_D with increasing formaldehyde concentration probably results from the effects of Equilibrium 6. In a recent paper [20], the change in the product from the reduction of acrylonitrile with concentration was monitored by noting that for a diffusion limited current, I_D/c is proportional to n (see Equation 7). Such an analysis cannot be fully justified in the case of formaldehyde reduction at room temperature because the reaction is not diffusion controlled. Clearly, the rate of reduction is kinetically controlled, but if the rate of generation of electroactive species is first order with respect to total formaldehyde concentration, it is to be expected that I_L/c would remain proportional to n. Hence in the final column of Table 1, I_L/c is reported and it can be seen that its value decreases above 10% formaldehyde. This may indicate a change in product from methanol ($n = 2$) to ethylene glycol ($n = 1$) with increasing formaldehyde concentration, although Equilibrium 6 will also influence I_L and hence I_L/c. The data in Table 1 also show a shift in half-wave potential and wave slope at very low concentrations; these may also be taken as an indication of a change in reaction mechanism. At the higher formaldehyde concentrations the wave slope is about (150 mV)$^{-1}$, probably indicating that the slow step in the electrochemical reduction of the free formaldehyde is the addition of the first electron to form an anion radical. At lower formaldehyde concentration, the Tafel slope is significantly lower as could arise if $n \rightarrow 2$.

The influence of some changes to the electrolyte medium were also investigated. i–E curves were recorded for 40% formaldehyde with sodium formate as the electrolyte before and after the addition of tetrabutylammonium ion to the solution. The responses are identical. At carbon cathodes, the addition of tetrabutylammonium ion has been reported to improve the current efficiency for ethylene glycol formation. This apparent discrepancy could arise if the carbon surface is a more effective catalyst for hydrogen evolution than mercury and the role of the tetraalkylammonium ion is to adsorb on the cathode surface and inhibit hydrogen evolution. This explanation was supported by experiments with the carbon microdisc electrodes available to us (they were manufactured from carbon fibres, but their surface characteristics are unknown). At these microelectrodes, no well formed reduction wave could be observed for formaldehyde reduction and hydrogen evolution commenced at less negative potentials. But it should also be recognized that the enhanced diffusion rate to microelectrodes means that the relative importance of mass transport and kinetically controlled reactions will not be the same at microelectrodes and at large planar electrodes. Hence, at least in some conditions, the ratio of H_2 evolution to HCHO reduction currents will be different at the two types of electrode.

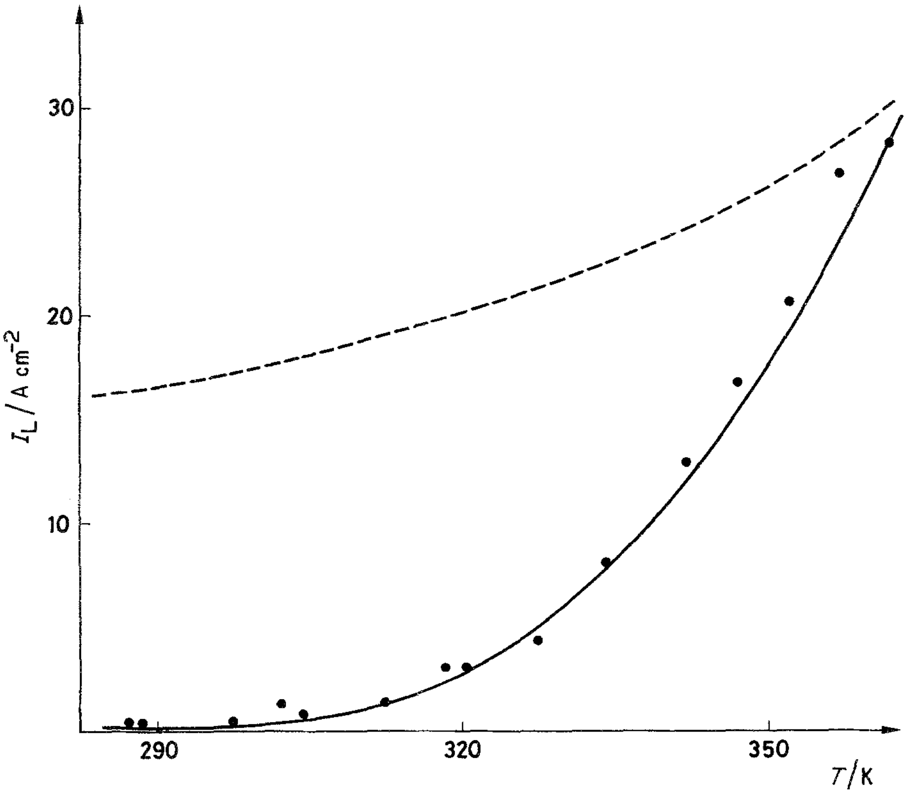


Fig. 2. Dependence of the limiting current density for 40% formaldehyde reduction on temperature, 1 mol dm^{-3} sodium formate, pH 7. Hg plated 10 μm Au microdisc electrode. The dashed line indicates the calculated mass transport limited current assuming $D = 5 \times 10^{-6}$ cm^2 s^{-1} at 293 K and the energy of activation for diffusion as 8 kJ mol^{-1}.

i-*E* curves at the mercury microelectrode also showed the limiting current density for the reduction of 40% formaldehyde to be independent of pH over the range 4 to 10. Below pH4, there was increasing interference from hydrogen evolution.

Finally, the effect on the system of increasing the temperature was studied. Well formed reduction waves were obtained for the reduction of 40% formaldehyde at all temperatures between 288 K and 363 K (there are no obvious signs of *iR* distortion despite the current densities reaching almost 30 A cm^{-2}). The most striking feature is the strong increase in the limiting current density with temperature; presentation of the data as a plot of log i_L against $1/T$ shows a liner relationship and leads to an energy of activation of 49 kJ mol^{-1}. This is a further confirmation that the limiting current is determined by the rate of a chemical step. The limiting current densities as a function of temperature are reported in Fig. 2. Also shown in the figure as a dashed line is the variation of the diffusion limited current density with temperature, calculated assuming that $D = 5 \times 10^{-6}$ cm^2 s^{-1} at 293 K and that the energy of activation for diffusion is 8 kJ mol^{-1}. It can clearly be seen that the observed limiting current density approaches the calculated diffusion limited current density with increasing temperature and, by 363 K, the difference is less than 10%.

Hence at 363 K the reduction of formaldehyde is close to diffusion controlled and, therefore, I_L/c should be proportional to n. Therefore, *i*-*E* curves were recorded for several concentrations of formaldehyde in 1 mol dm^{-3} sodium acetate, pH7, and the resulting data were used to construct the I_L/c against c plot shown in Fig. 3. The decrease in I_L/c with concentration and the change from $n = 2$ to $n = 1$ with increasing concentration is clearly demonstrated.

Hence these experiments with microelectrodes clearly demonstrate that chemical reactions such as the dehydration of formalin to form free formaldehyde, Equation 1, or the dimerisation of formalin, Equation 6, commonly determines its rate of reduction even with very concentrated formaldehyde solutions. Moreover, the results would suggest that, otherwise, the reduction of formaldehyde at mercury in neutral solutions is a straightforward reaction; the rate determining step in the reduction of the free formaldehyde is probably the formation of its anion radical and even at potentials in the limiting current plateau, there are no important competing electrode reactions.

The results also have important consequences for the design of electrosynthetic processes for ethylene

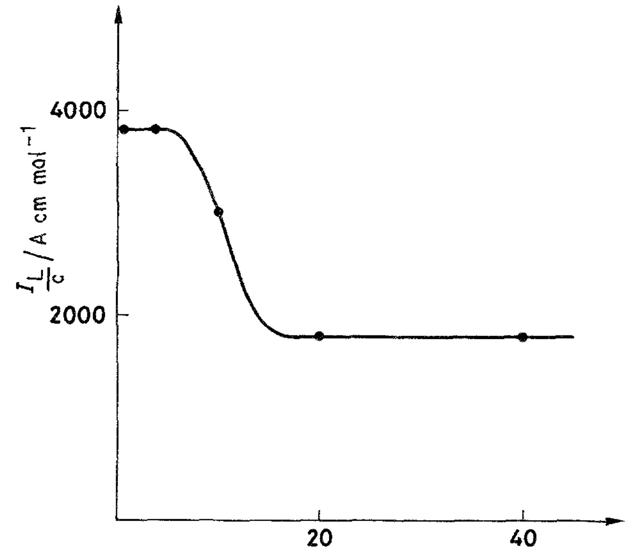


Fig. 3. I_L/c as a function % HCHO in 1 mol dm^{-3} sodium formate, pH 7. Hg plated, 10 μm diameter Au disc. Temperature 363 K.

glycol. First, they explain the necessity of using a high concentration of formaldehyde and demonstrate clearly the advantage of using an elevated temperature; the former favours the second order reactions of intermediates, whereas the latter ensures the formation of the electroactive free formaldehyde at a high rate. Similar reasoning leads to the conclusion that a high current density for formaldehyde reduction would lead to a high concentration of radical intermediates and hence to the dimeric product, ethylene glycol. Secondly, the data from the microelectrode experiments imply that with high formaldehyde concentrations, the reduction at mercury is a $1e^-$ process and hence, perhaps, that ethylene glycol should be formed in good yields at mercury (and, logically, similar metal) cathodes. The latter conclusion was investigated further.

3.2. *Electrosyntheses*

The influence of reaction conditions on the yield of ethylene glycol from the cathodic reduction of formaldehyde has been extensively studied and the details of this programme will be reported elsewhere [19]. Here, the purpose was only to check the influence of cathode material under otherwise favourable conditions. These include the use of sodium formate pH7 and also containing $(C_4H_9)_4N^+$, as the catholyte, a high temperature (353 K), and a high current density. Where possible a flow cell with a cation membrane was used for the electrolysis. With mercury, this design cannot be employed and in order to be certain that cell design was not a critical factor, two different glass cells were utilized and some experiments with other cathodes were repeated in the glass cell. The results of the preparative scale electrolyses are reported in Table 2. It can be seen very clearly that graphite is the cathode of choice, although significant ethylene glycol is formed at mercury. No ethylene glycol was detected after electrolyses at cadmium or lead cathodes. The experiments also confirm the advantage of the elevated temperature and of a high current density. The lower yield at the graphite felt probably also reflects the lower real current density at the very porous and high area material.

A further observation concerning the electrolyses at mercury should be noted: a considerable quantity of a grey solid was formed on the cathode surface. It was thought that this precipitate was an organomercury compound; attempts to convert it into ethylene glycol were not successful.

Table 2. Results of preparative scale electrolyses

Electrode	*I(mA cm^{-2})*	*$(C_4H_9)_4N^+$*	*Current efficiency (%)*
Graphite	10	Yes	42
	50	Yes	79
	250	Yes	87
	250*	Yes	55
Graphite felt ESC 1#GF-56	250	Yes	30
Mercury†	250	No	30
Lead‡	250	Yes	0
	250	No	0
Cadmium	250	Yes	0

Reduction of 40% formaldehyde to ethylene glycol in 1 mol dm^{-3} sodium formate, pH 7. Temperature 353 K. Electrolyses in MP flow cell.

* room temperature. † glass cells. ‡ MP and glass cell.

4. Discussion

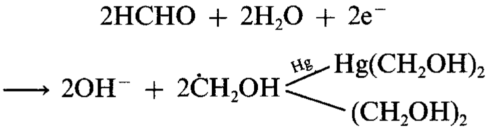
From the viewpoint of the development of a process for the synthesis of ethylene glycol, the conclusions of this study are very clear. Graphite is definitely the preferred and only viable cathode. The yield of ethylene glycol is much higher than at mercury. Moreover, since mercury is not possible as a cathode in most practical cell designs, the electrolyses were carried out at lead and cadmium, metals expected to give similar results to mercury. At these metals no ethylene glycol was found.

In comparing the results at the mercury microelectrode and the large mercury pool used for preparations, however, some differences should again be emphasized. The rate of diffusion to microelectrodes is much higher than to planar structures. Hence, in the solution conditions used for the electrosyntheses, the limiting current density at the microelectrode is 30 A cm^{-2}. Even with highly turbulent conditions this would be difficult to achieve in a synthesis cell and, in any case, it would be catastrophically detrimental to the performance of the membrane and to the energy efficiency/temperature control of the cell. Therefore it must remain speculation as to what the yield of ethylene glycol would be at 30 A cm^{-2}, a current density 120 times higher than the maximum used in the synthesis experiments.

It is also not certain whether the organomercury compound is an intermediate in the formation of ethylene glycol, that is

$$2HCHO + 2H_2O + Hg + 2e^- \longrightarrow 2OH^- + Hg(CH_2OH)_2 \longrightarrow Hg + (CH_2OH)_2 \quad (8)$$

or whether the formation of the organomercury compound is an unwanted side reaction, that is



$$2HCHO + 2H_2O + 2e^- \longrightarrow 2OH^- + 2\dot{C}H_2OH \begin{cases} \xrightarrow{Hg} Hg(CH_2OH)_2 \\ \longrightarrow (CH_2OH)_2 \end{cases} \quad (9)$$

The latter is more likely since ethylene glycol could not be formed from the solid formed during electrolysis and such chemistry is not known in the literature. It is certain that graphite cannot form an 'organometallic' product and it is also possible that the graphite is able to catalyse the dimerisation of the radicals to ethylene glycol.

In any case, we believe that the microelectrode experiments demonstrate clearly the change from $2e^-$ to $1e^-$ reduction at mercury with increasing formaldehyde concentration. Moreover, they provide perhaps the only method for probing the mechanism of this important new process and can be used to investigate the influence of temperature, pH, etc.

Acknowledgement

The authors thank Dr Norman L. Weinberg, The Electrosynthesis Co, for most helpful discussions about the chemistry and for access to presently unpublished data.

References

[1] K. Vesely and R. Brdicka, *Collect. Czech. Chem. Commun.* **12** (1947) 313.
[2] R. Bieber and G. Trumpler, *Helv. Chim. Acta.* **30** (1947) 706.
[3] R. Brdicka, *Coll. Czech. Chem. Commun.* **20** (1955) 387.
[4] *Idem, Z. Elektrochem.* **59** (1955) 787.
[5] N. Landquist, *Acta. Chem. Scand.* **9** (1955) 867.
[6] P. Valenta, *Coll. Czech. Chem. Commun.* **25** (1960) 853.
[7] M. A. Loshkarev and A. J. Tschernikov, *Russ. J. Phys. Chem.* **27** (1953) 1778.
[8] S. Clarke and J. A. Harrison, *J. Electroanal. Chem.* **36** (1972) 109.
[9] A. Calusaru, I. Crisan and J. Kuta, *ibid.* **46** (1973) 51.
[10] J. M. Los, A. A. A. M. Brinkman and B. C. J. Wetsma, *ibid.* **56** (1974) 187.
[11] J. M. Los, L. F. Roeleveld and B. C. J. Wetsma, *ibid.* **75** (1977) 819.
[12] P. G. Russell, N. Kovacs, S. Srinivasan and M. Steinberg, *J. Electrochem. Soc.* **124** (1977) 1329.
[13] A. P. Tomilov, E. L. Klyuev and V. D. Nechepornoi, *Russ. J. Gen. Chem.* **43** (1973) 2792.
[14] *Idem, ibid.* **11** (1975) 2010.
[15] H. Watanabe and M. Saito, *Toyo Soda Kenkyo, Hokoku* **24** (1979) 93.
[16] M. Saito and Y. Tokuyuma, German Pat. 3,018,844 (1980).
[17] N. L. Weinberg, US Pat. 4,478,694 (1984).
[18] N. L. Weinberg, M. Lipsztajn, D. J. Mazur, M. Reicher, H. R. Weinberg and E. P. Weinberg, in Recent Advances in Electroorganic Synthesis (edited by S. Torii) Elsevier (1987).
[19] N. L. Weinberg *et al.* to be published.
[20] M. I. Montenegro and D. Pletcher, *J. Electroanal. Chem.* **248** (1988) 229.