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Improved yields of oxalate, glyoxylate and glycolate from the electrochemical reduction of carbon dioxide in methanol

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The yields of oxalate and especially of glyoxylate and glycolate were enhanced by the use of methanol containing hydroxylamine and tetramethylammonium chloride in the controlled potential electrochemical reduction of carbon dioxide at a lead electrode. An eightfold increase in the solubility of CO_2 was found compared with water so that the initial concentration was 4.48×10^{-3} M. Products were mainly glyoxylate (up to 9.7×10^{-3} M at -2.0 V) and glycolate (up to 6.6×10^{-3} M at -2.3 V) with some oxalate (up to 1.3×10^{-4} M at -1.7 V) depending on the time and electrode potential. Very little formate was produced. Current densities were about 30 A m^{-2}.

1. Introduction

The electrochemical reduction of carbon dioxide has been studied since the 1960s [1]. In aqueous solutions the usual product is formic acid which can be further reduced to formaldehyde and thence to methanol and to methane [2]. However, aprotic solvents permit the formation of carbon monoxide [3] or oxalate [4,5]. Aylmer-Kelly *et al.* [6] and Lamy *et al.* [7] obtained evidence for the initial formation of a carbon dioxide radical anion. All these observations can be rationalized in the mechanism suggested by Gressin *et al.* [5] in Scheme 1. They used this mechanism to explain the results of their electrolytic reduction of CO_2 in DMF and DMSO with small amounts of added water, on both mercury and lead electrodes [5]. They obtained mainly oxalate, some carbon monoxide, occasionally some glycolate, but negligible hydrogen.

In a subsequent paper, Amatore and Saveant [8] considered the three competing Pathways 2, 3 and 4 in Scheme 1 using product distribution data together with kinetic data obtained by fast sweep cyclic voltammetry [7]. Three theoretical models were then developed to compare the relative rates and yields for this Scheme. In the first model, a function F_1, of the yields of formate, R_f, and of carbon monoxide, R_c, was related to the ratio of water to carbon dioxide via rate constants k_2 and k_3, as follows:

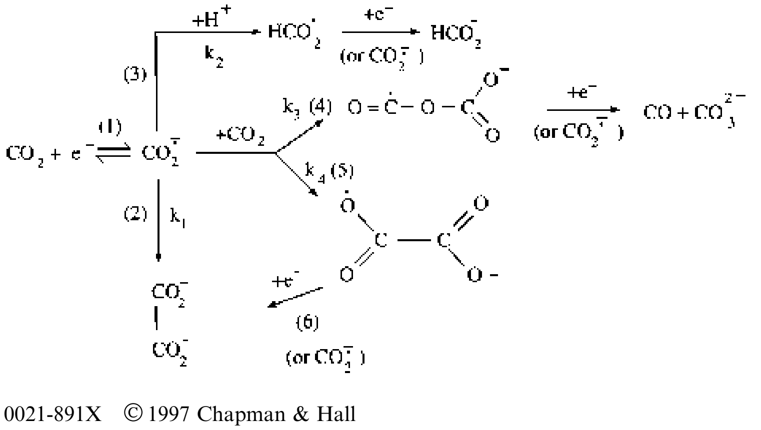
$$\begin{aligned} F_1 &= 2(R_f/R_c)[1-(i_o/i_l)/(1+R_f)] \\ &= (k_2/k_3)\times[H_2O]/[CO_2] \end{aligned} \qquad (1)$$

where i_o is the imposed current and i_l is the current on the plateau of the wave; $i_l = FAD[CO_2]/\delta$ where A is the electrode area, D the diffusion coefficient of CO_2 and δ the diffusion layer thickness. A graph of F_1 against $[H_2O]/[CO_2]$ was linear with a slope giving $k_2/k_3 = 0.24$

The second more complex function, F_2, related these quantities to the relative yield of oxalate, R_o, in the form $R_o/(1 + R_f)$. Thus,

$$\begin{aligned} F_2 &= \{1+2R_f/R_c[1-(i_o/i_l)/(1+R_f)]\}^{-3/2} \\ &\quad \times \frac{(D/2[CO_2])^{1/2}}{\delta} \times (i_o/i_l) \end{aligned} \qquad (2)$$

From a graph of $R_o/(1 + R_f)$ against log F_2, they deduced that $k_1/k_3{}^{-3/2} = 56$ $M^{1/2}$ $s^{1/2}$.



Scheme 1. Mechanistic routes for the electrochemical reduction of carbon dioxide to oxalate (2) or (5); formate (3) or carbon monoxide (4) (after Gressin *et al.* [5]).

In the third model they considered the possibility of oxalate formation via CO_2 radical–molecule coupling (Scheme 1, Equation 5), as originally suggested by Aylmer-Kelly *et al.* [6]. ε is the fraction of radical–radical dimerization (Scheme 1, Equation 2) and $(1 - \varepsilon)$ is the fraction of radical–molecule coupling (Scheme 1, Equation 5). F_2 was modified by replacing R_o with $R_E = R_o - [(1 - \varepsilon)/\varepsilon\,]R_c$, replacing R_c with R_F, $= R_c/\varepsilon$, and k_2/k_3 with $k_2/\varepsilon k_3$. The best fit of log $k_1/k_3^{-3/2}$ against ε was found at $\varepsilon = 1$. Thus C–C coupling of CO_2^{-}. with CO_2 appears to be neglible as a pathway to oxalate, contrary to Aylmer-Kelly *et al.* [6].

Amatore and Saveant used a value for k_1 of 10^{-7} $\text{M}^{-1}\ \text{s}^{-1}$ from earlier work [7] to give values of $k_2 = 7.7 \times 10^2$ and $k_3 = 3.2 \times 10^3$. These values confirmed that the direct dimerization route (Scheme 1, Equation 2) predominated over step 3 (protonation to formate) and step 4 (formation of carbon monoxide via C–O coupling), and that step 5 can be ignored.

An interesting variation was discovered by Bewick and Greener [9, 10], confirmed by Wolf and Rollin [11] and has been further developed by ourselves [12, 13]. If the reduction is carried out in aqueous solutions containing tetraalkylammonium salts, not only is oxalate formed at the expense of formate [12, 13], but further reduction products from oxalate such as glyoxylate [12–14], glycolate [9,14], tartrate[13, 14] and malate[10] have been detected. An overall reaction scheme involving these species was suggested by ourselves in 1980 [12] and is shown in Scheme 2.

Although the oxalate is substantially ionized, at pH 9–10, the initial step in its reduction will be protonation by the solvent away from the electrode[15], followed by an electron transfer. The resulting dianion radical could dimerize to tartrate or more likely accept another proton to form a dihydroxy radical which could dimerize to tartrate, or be reduced with a second electron. The resulting dianion might protonate directly or rearrange with a proton shift followed by a further protonation to the hydrated form of glyoxylate, which is known to predominate in equilibrium with the aldehyde form [16]. Reduction of glyoxylate to glycolate follows the usual e H e H mechanism. The rate of glyoxylate reduction is limited by the dehydration equilibrium of the hydroxylated glyoxylate [16]. Voltammetric studies of carbon dioxide [17,18], of oxalate [15] and of glyoxylate [16], as well as the electrochemical reduction of glyoxylate[19] have helped to elucidate the reaction mechanisms. Photocatalytic studies using semiconductor colloids have given similar results [14,20,21].

One of the problems with this route is caused by the low solubility of carbon dioxide in water, especially as the pH has to be kept high in the range 9–10. If it is not kept high, then the carbon dioxide radical anions are easily protonated giving only formate. It has generally been observed that only free carbon dioxide molecules can be electrochemically reduced [22, 23], but not carbonate or bicarbonate. The problem with having low solubility of CO_2 is that the reaction rate and hence the current density is kinetically limited by the protonation–dehydration process of bicarbonate[18]:

$$HCO_3^- + H^+ \overset{K}{\rightleftharpoons} H_2CO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO_2 + H_2O$$

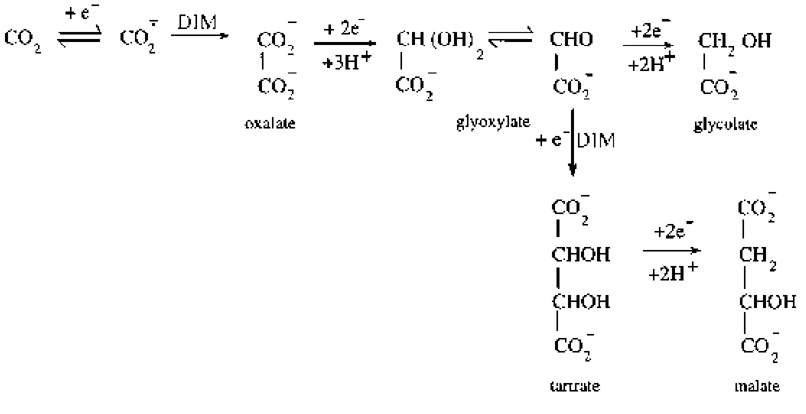
If $k_1 > k_{-1}$, then $d[CO_2]/dt = Kk_1[HCO_3^-][H^+]$. Alternatively,

$$HCO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO_2 + OH^-$$

so, if $k_2 > k_{-2}$, then $d[CO_2]/dt = k_2[HCO_3{}^-]$

In aqueous solutions of pH 8–10 these two mechanisms compete, the latter dominating at the higher pH[18]. The total carbonate plus carbon dioxide was usually about 4×10^{-3} M, whereas electrochemical data indicate that the effective free carbon dioxide concentration is 10^{-4} to 10^{-6} M. Of course if CO_2 is bubbled through the reaction mixture, the above reactions may not be in equilibrium, and the effective free CO_2 may be much higher. Even so the observed current densities around 30 A m^{-2}[17], are rather low for practical purposes.

In an alternative approach Mahmood *et al.* [24,25] used a gas diffusion electrode. This gave current densities of up to 1150 A m^{-2} for the formation of formate on lead at pH 2.0 with up to 100% current efficiencies.



Scheme 2. Reaction scheme for the electrochemical reduction of carbon dioxide to two and four carbon products (after Bennett *et al.* [12]).

It was decided to try alternative protic solvents, in which CO_2 might be more soluble. The results of these studies are reported here.

2 Experimental details

2.1 *Solubility of carbon dioxide*

The solubility of carbon dioxide was determined in a number of solvent systems. Each solvent was purged with oxygen free nitrogen, then carbon dioxide which had been purified through a vanadium[II] train was bubbled through it for 30 min to saturate the solution. The carbon dioxide concentrations were determined by the addition of standard barium hydroxide solution and back titration with standard oxalic acid solution as described previously[12,19]. Solvents tested were: water, methanol, ethanol, propan-1-ol, propan-2-ol, ethane-1,2-diol and methanol containing hydroxylamine hydrochloride (1.43 % and 3.09 %).

2.2 *Electrochemical reactions*

The controlled potential electrolyses were carried out in a perspex dialysis cell with a pure lead sheet (0.1 mm thick, area 20.9 cm^2) inserted between sections of the cell as described previously [12, 19]. The compartments were separated by a cation exchange membrane. A silver–silver chloride reference electrode and a platinum foil counter electrode were used. The cathode compartment had a volume of 70 cm^3 and was fitted with a stirrer. A Witton T6 tutorial potentiostat was used to control the potential.

Hydroxylamine hydrochloride (BDH) (3 g) was dissolved in methanol (BDH Analar) (100 cm^3). This solution was then made 0.1 M in tetramethylammonium chloride (BDH). It was deaereated with oxygen-free nitrogen (15 min), and then carbon dioxide, which had been purified through a vanadium (II) train, was bubbled through it. Finally, the pH of the solution was adjusted to pH 10 with tetramethylammonium hydroxide solution (25 % aqueous solution BDH).

The solution was electrolysed at a range of potentials: −1.7 V, −1.9 V, −2.0 V and −2.3 V for up to 2.5 h. The current was monitored regularly to enable the average current density to be calculated.

2.3 *HPLC analysis*

At 30 min intervals 2 cm^3 samples were removed and passed through an ion-exchange column to remove tetramethylammonium ions. The eluate from each sample was collected, made up to 25 cm^3 and subjected to separate HPLC analysis on an Altex model 30 isocratic liquid chromatograph by the injection of 25 μL on to the 300 mm × 7.8 mm Aminex HPX-87 column, and eluting with 0.016 M H_2SO_4 at a flow rate of 0.3 $cm^3\ min^{-1}$. The detector was a Pye Unicam PU 4020 u.v. detector set at 210 nm. The peak areas were integrated with a Shimadzu C-R3A chromatopac integrator, and were standardized both qualitatively and quantitatively against authentic samples of formic, oxalic, glyoxylic, glycolic, tartaric, malic and succinic acids. A typical HPLC of standards is shown in Fig. 1.

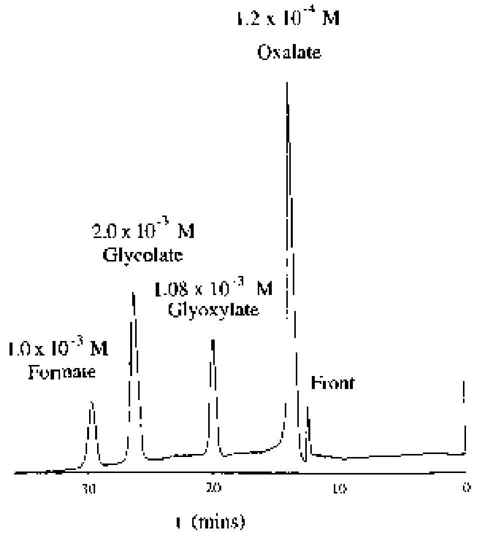


Fig. 1. High performance liquid chromatogram of formic, oxalic, glyoxylic, glycolic on an Aminex HPX-87 ion exchange column, eluted by 0.016 M H_2SO_4 with u.v. detection at 210 nm.

2.4 *Current efficiency calculations*

The theoretical charge (in coulomb) used, based on the product yields and Faraday's laws were obtained as follows:

$$Q_i = n_i F c_i V = (2Fc_f + 2Fc_o + 4Fc_{gx} + 6Fc_{gc})V$$

where c_f, c_o, c_{gx} and c_{gc} are the observed concentrations in mol dm^{-3} of formic, oxalic, glyoxylic and glycolic acids, respectively; $F = 96\,480\ C\ mol^{-1}$ and V is the volume of the reaction cell in dm^3.

The actual charge used from current measurements were given by

$$\begin{aligned} Q_t &= j_i A t_i \\ &= (j_1 + j_2 + \ldots + j_i) \times 2.09 \times 10^{-3} \times 30 \times 60\,C \end{aligned}$$

where j_i is the current density (A m^{-2}), A is the electrode area (m^2) and t_i is the time interval (s).

$$\text{Hence, current efficiency} = \frac{Q_i}{Q_t} \times 100\,(\%)$$

The yields shown in Table 2 are cummulative yields over the total time. For example, for the electrolysis at −1.9 V, after 120 min:

$$\begin{aligned} Q_i = {} & (2F \times 5.98 \times 10^{-6} + 2F \times 6.01 \times 10^{-5} \\ & + 4F \times 6.16 \times 10^{-3} \\ & + 6F \times 2.79 \times 10^{-3}) \times 0.07 = 280\ C \\ Q_t = {} & (19 + 21 + 23 + 24) \\ & \times 2.09 \times 10^{-3} \times 1800 = 327\ C \end{aligned}$$

Hence, current efficiency = (280/327)×100 = 86 %.

2.5 *GCMS analyses*

For the GCMS analyses, stock solutions of each standard were made by taking 50 mg or 100 mg in diethylether (100 cm^3). To the stock solution (2 cm^3) were added triethylamine (0.2 cm^3), N-methyl-N-tertiary-butyldimethylsilyltrifluoroacetamide (MTBSTFA) [26] (0.2 cm^3) and isooctane (0.2 cm^3). All samples of C4 or more were sealed in a vial and heated at 60 °C for 4 h. The products were extracted with ether, diluted and an aliquot (2 μL) was injected into the GC–MS. This consisted of a 25m Hewlett Packard 5890 capillary column packed with 14% cyanopropyldimethyl siloxane, with helium carrier gas using a temperature programme, 3 min at 70 °C, then increasing at 10 °C per minute up to 240 °C. The detector was Hewlett Packard 5970 quadrapole mass spectrometer, scanning over *m*/*e* 29–700. Data were processed in a Hewlett Packard 9000 computer series 200.

3. Results

The solubilities of carbon dioxide in different protic solvents are shown in Table 1. On going from water to methanol there is a nearly threefold increase in solubility. Although all the other pure solvents show an increased solubility compared with water, none of them are as good as methanol. Addition of hydroxylamine to the methanol caused a further increase in solubility up to eightfold. This solution was therefore used for the electrolyses.

Attempts to carry out voltammetry of carbon dioxide in these methanolic solutions were singularly unsuccessful. The reason for this was not discovered. Indeed, when voltammetric reduction of carbon tetrachloride in methanol was attempted as a control, again no reduction waves were observed. Naitoh *et al.* obtained some Tafel plots with carbon dioxide in methanol [28]. Therefore, controlled potential electrolyses were carried out over a range of potentials close to those observed voltammetrically for the reduction of carbon dioxide to glyoxylic acid in aqueous tetramethylammonium chloride at pH 10 [13].

Table 1. Solubilities of carbon dioxide

Solution	*CO_2 concentration*/g dm^{-3}
Water	25.8
Methanol	67.6
Ethanol	47.0
Propan-1-ol	39.4
Propan-2-ol	40.5
Ethane-diol	14.5
Methanol/hydroxylamine (1.44%)	110.5
Methanol/hydroxylamine (3.09%)	197.3

The products of the electrolyses were analysed by HPLC. Attempts were made to derivatize the reaction mixture for GCMS analysis with MTBSTFA, which readily forms volatile derivatives of organic acids at 60 °C [26]. Other silylating agents such as bistrimethyltrifluoroacetamide require heating up to 160 °C. These were not successful, despite the successful formation of standards of each likely product and analysis by GCMS. The problem depends on extracting the analyte into an aprotic medium: in this case, ether with added isooctane. When the electrolysis was carried out in an aprotic solvent (acetonitrile) this procedure was successful. Oxalate was the sole product, as characterized by GCMS.

Current efficiencies were calculated for each 30 min interval cummulatively. The ranges of products at each potential and selected times are shown in Table 2, together with the current densities and current efficiencies. Oxalate is the major product at short times, then glyoxylate is formed. At longer times glycolate is also found. This is seen at all three lower potentials. Then at −2.3 V glycolate alone is the major product. Small amounts of formate are formed at all potentials.

Table 2. Electrolytic reduction products from carbon dioxide (initial concentration: 4.48×10^{-3} M)

$-E$/V	*Time*	*Oxalate*	*Formate*	*Glyoxalate*	*Glycolate*	j/Am^{-2}	*C.E.*/%
1.7	30	12.5	0.0	0.0	0.0	8	6
1.7	120	4.3	2.7	138	33.8	12	35
1.9	30	5.4	0.8	5.8	0.0	19	3
1.9	60	1.9	1.0	31.3	13.8	21	10
1.9	90	0.8	2.2	141	61.1	23	27
1.9	120	0.6	3.3	616	279	24	86
1.9	150	0.3	6.0	295	754	31	91
2.0	30	7.3	0.0	10.3	22.5	21	16
2.0	60	3.1	2.3	43.5	81.3	22	28
2.0	90	1.2	3.1	294	286	24	78
2.0	120	0.7	6.6	972	566	25	142
2.3	30	0.0	7.4	0.0	16.5	19	13
2.3	60	0.0	1.5	0.0	52.2	21	14
2.3	90	0.0	3.1	0.0	123	22	22
2.3	120	0.0	4.8	0.0	659	24	83

Product concentrations are $\times 10^5$ mol dm^{-3}

The best yields were at −2.0 V after 2 h, when the concentration of glyoxylate was 9.72×10^{-3} M and of glycolate 5.66×10^{-3} M with an apparent overall current efficiency of 142%. The current density was 25 A m^{-2}.

At −1.9 V and 2 h the current efficiency was more realistic at 91% and current density higher at 31 A m^{-2}, but the yield of glyoxylate was lower at 3.0×10^{-3} M and glycolate highest at 7.5×10^{-3} M. Interestingly, at the same potential, after only 2 h the yield of glyoxylate was higher at 6.16×10^{-3} M, and that of glycolate lower at 2.79×10^{-3} M, with a similar current efficiency of 86%.

4. Discussion

The problem of the low solubility of carbon dioxide in protic media such as water was greatly improved by switching to a different solvent. The best among those tried was methanol, in which carbon dioxide is 2.6 times as soluble. This solubility was further enhanced by the addition of up to 3.0 g hydroxylamine hydrochloride to 100 cm^3 of methanol. This increased the solubility to 7.6 times that in water.

The solution also contained tetramethylammonium chloride, and was operated at pH 10, which were the optimum conditions for the best yields of dimeric products such as oxalate and glyoxylate as previously described [12, 13]. In order to maximize the formation of glyoxylate, we operated in the potential range indicated by our voltammetric studies [12, 13] at which glyoxylate is the major product in water: −1.7 to −2.3 V.

It can be seen from Table 2 that at short times and lowest potentials only oxalate is formed, in accordance with reaction Scheme 2. As time progressed the oxalate concentration decreased as it was converted to glyoxylate, whose concentration then steadily increased, until at still longer times glycolate was formed at the expense of glyoxylate.

As expected some formate was usually produced due to the direct protonation of the carbon dioxide radical anion and further reduction. We did not look for alternative products such as carbon monoxide or hydrogen, which others have sometimes found [23,27,28] and which could contribute to the overall faradaic yield.

The progress of the reaction is also illustrated in Figs 2 and 3 showing the logarithm of the yields of the products against time for $E = -1.9$ V and $E = -2.0$ V. The pattern is characteristic of consecutive reactions:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

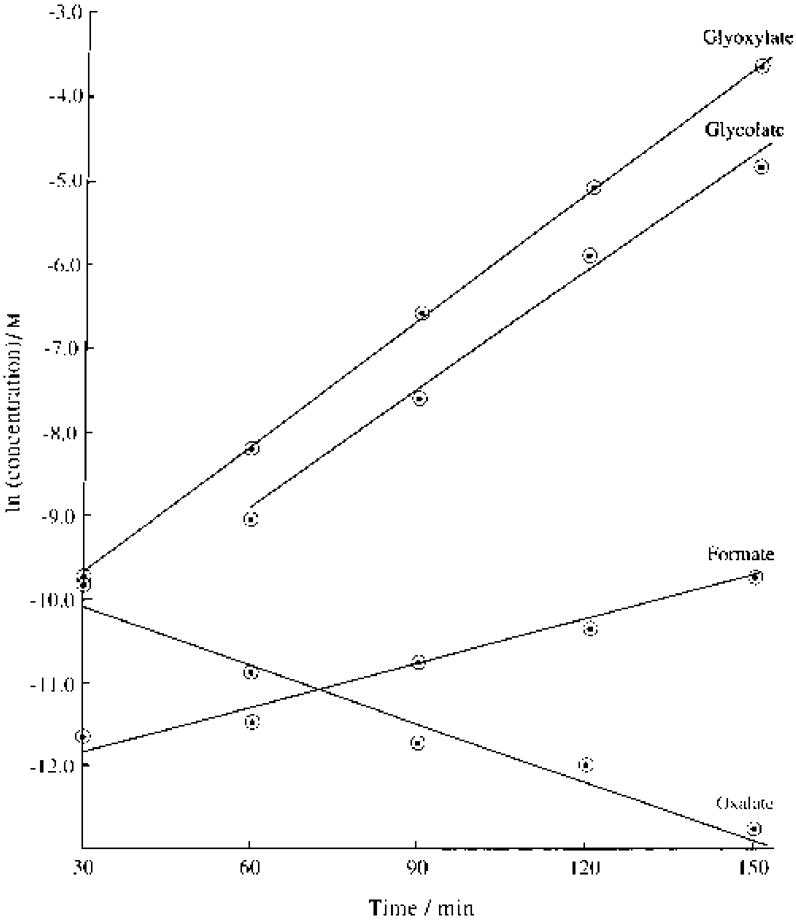


Fig. 2. Graph of ln(concentration) of products against time for the electrochemical reduction of carbon dioxide in methanolic tetramethylammonium chloride containing 3% hydroxylamine on a lead cathode at −1.9 V vs. Ag/AgCl.

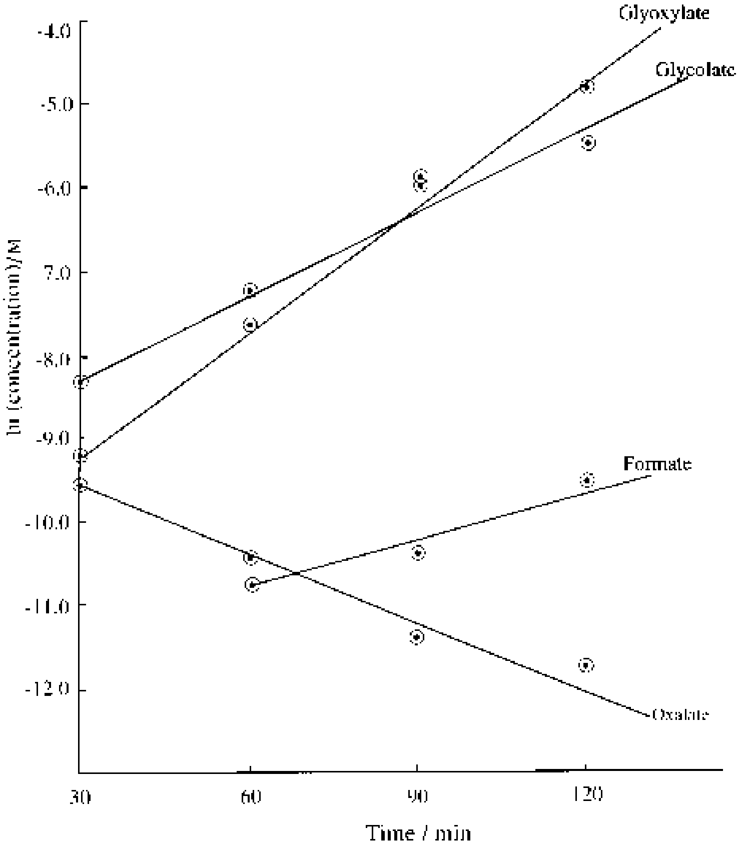


Fig. 3. Graph ln(concentration) of products against time for the electrochemical reduction of carbon dioxide at −2.0 V vs. Ag/AgCl. (Other conditions as in Fig.2.)

The relative values of k_1, k_2 and k_3 at the different potentials can be deduced from the data. At −1.7 V, $k_1 > k_2$, which is rate limiting, whereas at −1.9 V and − 2.0 V, $k_1 < k_2 = k_3$. At −2.3 V, $k_1 < k_2 < k_3$ as no oxalate or glyoxlate were detected, indicating that k_3 is now rate limiting. This is approximately the condition under which Bewick and Greener obtained glycolate [9]. They used a lead electrode, aqueous tetraalkylammonium salts and a fairly negative potential: −2.6 V.

In these experiments tartrate was not obtained, in contrast to our similar experiments on the electrochemical reduction of glyoxylate [19], and photoelectrochemical reduction of carbon dioxide [14]. In the former case with a lead electrode at pH 2.1 the yield of glycolate:tartarte was 95%:5%. At pH 9.0 on lead, similar to the present conditions, the ratio was 34%:65%. Only on a carbon electrode was the yield from glyoxylate almost exclusively glycolate at all pHs. No malic acid was detected in this work or in that with glyoxylate.

The use of this particular solvent mixture produced a very similar current density, up to 31 A m^{-2}, to that obtained in purely aqueous media[13] (30 A m^{-2} at −1.88 V). Although Naitoh *et al.* [27] quote faradaic efficiencies for their electrochemical reductions in methanol, they do not quote any current densities. Mahmood *et al.* [24] obtained very much higher current densities using lead-impregnated PTFE-bonded carbon gas-diffusion electrodes in aqueous dilute sulfuric acid (up to 115 mA cm^{-2} with up to 100% current efficiency of formic acid, under controlled current mode). But they observed no dimeric products.

In the paper by Naitoh *et al.*[27] describing the electrochemical reduction of CO_2 in methanol and in methanol/water mixtures, the supporting electrolyte was reported to be alkyldimethylbenzylammonium chloride (8 mM) and the electrode was copper, as used by Hori *et al.*[29,30]. The gaseous products were measured by gas chromatography with helium as carrier gas. The products reported were H_2, CO, CH_4, C_2H_4 and sometimes C_2H_6. No reference was made to the possibility of nonvolatile products (not even formate). It is not clear how faradaic efficiencies were calculated, as no current or coulombic data are given. Overall efficiencies reported varied from 45% to 126%. Hydrogen was given as the major component (42% to 120%). The best yields of carbon containing products were 19.3% for CO in pure methanol at −2.1 V. Under the same conditions ethene was reported as 4.3%. When water was added the yields of these carbon-containing volatile products diminished. In our system the best current efficiencies overall were 91% at −1.9 V (ignoring the one apparent value of 142% at −2.0 V). As with Naitoh *et al.* [27] the current efficiencies increased as the applied voltage increased up to the maximum.

The aim of this work was to improve the yields of dimerized products. It was clear from Gressin's

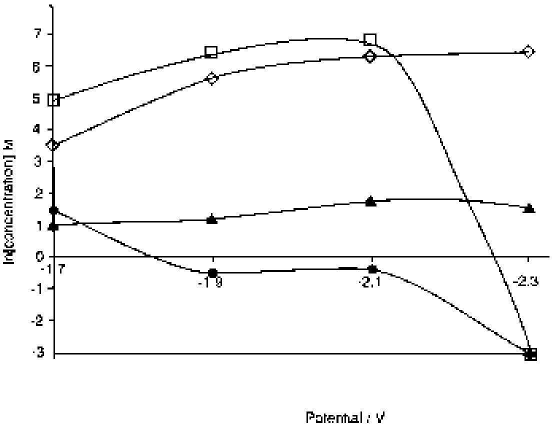


Fig. 4. Effect of potential on product yields after 120 min reduction. (Other conditions as in Fig. 2.) Key: (□) glyoxylate, (◇) glycolate, (▲) oxalate and (●) formate.

results [5] and those of others [23] that under our conditions at pH 9–10, no hydrogen would be produced. Although Gressin obtained up to 25% of carbon monoxide on mercury, yields on lead were never more than 7–9%, and then only with considerable water present. Other workers similarly found negligible carbon monoxide at lead electrodes[28]. Thus, it is unlikely that the low current efficiencies at the shorter times were due to the formation of hydrogen or carbon monoxide. It is more probable that a background process, such as the reduction of an impurity, perhaps from hydroxylamine, was occurring, which decreased progressively as the impurity was removed. Naitoh *et al.* [27] observed a similar effect, perhaps also from their unusual supporting electrolyte.

The methanol acts not only as the solvent but also as a weak proton donor, buffered by the hydroxylamine. It is always hard to predict solvent effects, as there is usually a close balance between similar energy terms. Additionally the entropy terms have a large influence [31]. Although enhanced solubility was obtained, there was little change in the current densities compared with aqueous solutions [13].

By changing the electrolysis potential it was possible to switch the major product from oxalate to glyoxylate and to glycolate all with particularly good yields, as shown in Table 2. Figure 4 shows the effect of the changing potential on the relative yields of products at 120 min. The use of methanol containing hydroxylamine hydrochloride, as well as tetramethylammonium chloride, resulted in greatly improved yields of glyoxalate, up to twenty fold, compared with earlier results in aqueous solutions [13]. Glycolate was regularly produced in similar high yields. Much lower amounts of formate were produced in the methanolic solutions.

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