Mechanism of the electrochemical reduction of carbon dioxide at inert electrodes in media of low proton availability

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Direct electrolysis of CO₂ in DMF at an inert electrode, such as mercury, produces mixtures of CO and oxalate, whereas electrolysis catalysed by radical anions of aromatic esters and nitriles produces exclusively oxalate in the same medium. Examination of previous results concerning the direct electrochemical reduction and the reduction by photoinjected electrons reveals that there are no significant specific interactions between reactant, intermediates and products on the one hand, and the electrode material on the other, when this is Hg or Pb. These observations and a systematic study of the variations of the oxalate and CO yields with temperature and CO₂ concentration, allow the derivation of a consistent mechanistic model of the direct electrochemical reduction. It involves the formation of oxalate from the coupling of two CO₂ radical anions in solution. CO (and an equimolar amount of carbonate) is produced by reduction at the electrode of a CO₂−−−−CO₂−−−− adduct, the formation of which, at the electrode surface, is rendered exothermic by non-specific electrostatic interactions.

Albeit a very stable molecule, carbon dioxide plays the role of a carbon source in essential natural processes. Among the artificial modes of activating this molecule, much attention has been devoted to electrochemical activation. The electrochemical generation of the CO₂ radical anion requires a fairly negative potential (the standard potential of the CO₂/CO₂−−−− couple in N,N’-dimethylformamide (DMF) with 0.1 mol dm⁻³ NEt₃ClO₄ as supporting electrolyte has been estimated to be −2.21 V vs. SCE by cyclic voltammetry on a mercury electrode.¹ The products of the direct electrochemical reduction depend on the chemical nature of the electrode and the reaction medium. In low acidity solvents, such as DMF, and with a mercury or lead electrode, the reduction takes place at potentials around the standard potential of the CO₂/CO₂−−−− couple indicating that the interactions between the electrode and the reactant, intermediates and products are weak. At such inert (or outersphere) electrodes, the reduction products are oxalate and carbon monoxide when the solvent is dry.²⁻³ Similar results were found in other aprotic solvents at Hg, Pb and TI electrodes.⁴ The relative amounts of oxalate and carbon monoxide depend upon current density and CO₂ concentration, and the presence of water promotes the formation of formate.² Other metals presumably play a catalytic role through chemisorption of CO₂, intermediates or products. CO is then the main product as with Au, Pt, Ag and Cu in propylene carbonate.⁴ This is also the case with Au, Sn, Cd and Zn layers freshly deposited on the electrode surface in DMF or N-methylpyrrolidone.⁵

In water, high yields of formic acid may be obtained as discovered many years ago⁶⁻⁸ and confirmed by more recent studies.⁹ However, the product distribution depends considerably upon the nature of the electrode material and the reaction medium, and chemisorption of intermediates and/or products also probably plays a crucial role. Besides formate and CO₂, other products such as formaldehyde,¹² methanol¹²,¹⁴ and methane¹⁴⁻¹⁸ can be formed. It is however, interesting to note that on an inert electrode such as lead, one obtains, with a large overpotential, solely formate,¹⁹ as expected from the results obtained in DMF. On the other hand, oxalate, partially reduced to glyoxalate, is formed, together with formate, on mercury in the presence of quaternary ammonium salts, again with a large overpotential.²⁰,²¹

The product distribution found in DMF at inert electrodes such as Hg and Pb, and its variations with current density and CO₂ concentration suggested the mechanism depicted in Scheme 1.²,²²⁻²⁴ Oxalate is considered to be formed from the coupling of two CO₂ radical anions [reaction (1)] while the production of CO₂ and of an equimolar amount of carbonate, involves, as intermediate, an adduct between CO₂ and its radical anion where the C−O bond formed results from the donation of an electron pair from the latter to the former [reaction (2)]. The secondary radical anion thus produced may successively undergo electron transfer from the electrode or from the primary radical anion accompanied by the breaking of one of the C−O bonds of the primary radical anion to yield CO₂ and carbonate [reactions (3) and (3’)]. The formation of formate involves the water that is present which may protonate CO₂−−−− leading to a neutral radical [reaction (4)]

(0) CO₂ + e⁻ → CO₂−−−−
(1) 2 CO₂−−−− → C=C=O, 0−−−−
(2) CO₂−−−− + CO₂ ⇌ O−−−−C0=O−−−−
(3) O=C−−−− + e⁻ → CO + CO₂−−−−
(3’) O=C−−−− + CO₂−−−− → CO + CO₂−−−− + CO₂
(4) CO₂−−−− + H₂O ⇌ HCO₂−−−− + OH⁻
(5) HCO₂−−−− + e⁻ → HCO₂⁻−−−−
(5’) HCO₂⁻−−−− + CO₂−−−− → HCO₂−−−−

Scheme 1
from which formate is derived after an additional electron transfer step [reactions (5) and (5')].

It has been found recently that radical anions of aromatic esters and nitriles may be used to catalyse homogeneously the electrochemical reduction of CO\textsubscript{2}. Over an extended range of concentration and temperature, the only reduction product is oxalate while no detectable amounts of CO are formed. This striking difference in product distribution between the direct and homogeneously catalysed reactions prompted us to re-examine the mechanism of the direct electrochemical reduction of CO\textsubscript{2} at inert electrodes. For this reason we analysed in a more systematic manner the effect of CO\textsubscript{2} concentration on product distribution. We also investigated the effect of temperature. The discussion will take into account the contention, based on Tafel plots and photoemission experiments, that specific adsorption is an essential factor of the reduction mechanism, even for electrodes previously presumed inert such as mercury and lead, in water\textsuperscript{26} as well as in aprotic solvents.\textsuperscript{27} The main questions to be addressed are: is the product distribution entirely controlled by homogeneous follow-up reactions; is the electrode surface playing a specific (chemical) role?

### Experimental

#### Chemicals

DMF (Carlo Erba, RPE) was kept over anhydrous Na\textsubscript{2}CO\textsubscript{3} for several days and stirred occasionally. It was then fractionally distilled under reduced pressure under N\textsubscript{2} twice and stored in a dark bottle under N\textsubscript{2}. In order to remove as much residual water as possible the solvent was repeatedly percolated before use through a column of neutral alumina (Merck, activity grade 1) previously activated overnight at 360\degree C under vacuum. Tetraethylammonium perchlorate (Fluka purum) was recrystallized twice from a 2:1 water–ethanol mixture and then dried in a vacuum oven at 60\degree C. CO\textsubscript{2} (99.998%) was supplied by SIAD (Italy). The solubility of the gas in DMF (0.199 mol dm\textsuperscript{-3} at 25\degree C and 1 atm pressure) at various temperatures and various partial pressures has been reported previously.\textsuperscript{28} DMF solutions containing various concentrations of CO\textsubscript{2} were prepared by saturating the solvent with appropriate mixtures of CO\textsubscript{2} and argon. The apparatus used for the preparation of the gas mixtures and the method of calculating CO\textsubscript{2} concentrations in the solution from its partial pressure in the gas phase have been described previously.\textsuperscript{28}

#### Electrochemical instrumentation and procedures

Cyclic voltammetric measurements were made with a PAR Model 173 potentiostat or with a home-built potentiostat equipped with positive feedback compensation.\textsuperscript{29} A programmable function generator Amel or a Model 568 EGG PAR 175 signal generator and a 2090 Nicolet oscilloscope. An Amel Model 863 X–Y recorder or an IFLELEC 2502 chart recorder were used for recording the cyclic voltammograms. A mercury micro-electrode was used as working electrode and a platinum wire as counter-electrode. The working electrode was made from a 2 mm diameter platinum sphere coated with mercury after electrolytic deposition of silver on a 1 mm diameter gold disk coated with mercury. The reference electrode was Ag/AgCl/Bu\textsubscript{4}NI (0.1 mol dm\textsuperscript{-3} in DMF) whose potential was made from a 2 mm diameter platinum sphere coated with platinum wire as counter-electrode. The working electrode mercury micro-electrode was used as working electrode and a recorder were used for recording the cyclic voltammograms. A Amel Model 863 X-Y recorder or an IFELEC 2502 chart equipped with positive feedback compensation,\textsuperscript{30} a programmable function generator Amel or a Model 568 EGG Model 173 potentiostat or with a home-built potentiostat.

Electrochemical instrumentation and procedures

Cyclic voltammetric measurements were made with a PAR Model 173 potentiostat or with a home-built potentiostat equipped with positive feedback compensation.\textsuperscript{29} A programmable function generator Amel or a Model 568 EGG PAR 175 signal generator and a 2090 Nicolet oscilloscope. An Amel Model 863 X–Y recorder or an IFLELEC 2502 chart recorder were used for recording the cyclic voltammograms. A mercury micro-electrode was used as working electrode and a platinum wire as counter-electrode. The working electrode was made from a 2 mm diameter platinum sphere coated with mercury after electrolytic deposition of silver on a 1 mm diameter gold disk coated with mercury. The reference electrode was Ag/AgCl/Bu\textsubscript{4}NI (0.1 mol dm\textsuperscript{-3} in DMF) whose potential was always compared with that of the working electrode. For this reason we analysed in a more systematic manner the effect of CO\textsubscript{2} concentration on product distribution. We also investigated the effect of temperature. The discussion will take into account the contention, based on Tafel plots and photoemission experiments, that specific adsorption is an essential factor of the reduction mechanism, even for electrodes previously presumed inert such as mercury and lead, in water\textsuperscript{26} as well as in aprotic solvents.\textsuperscript{27} The main questions to be addressed are: is the product distribution entirely controlled by homogeneous follow-up reactions; is the electrode surface playing a specific (chemical) role?

### Results

Fig. 1 shows a typical cyclic voltammogram of CO\textsubscript{2} in DMF. The cathodic peak remains irreversible up to 1000 V s\textsuperscript{-1}. The peak width indicates that electron transfer is rate-controlling with a transfer coefficient close to 0.5 (0.55). It has been reported that some reversibility appears at a high scan rate (4400 V s\textsuperscript{-1}) from which an approximate estimate of the standard potential of the CO\textsubscript{2}/CO\textsubscript{2}\textsuperscript{-} couple (−2.21 V vs. SCE in DMF +0.1 mol dm\textsuperscript{-3} Bu\textsubscript{4}NClO\textsubscript{4}) was derived.\textsuperscript{31} In the original publication, a rough estimate of 10\textsuperscript{17} mol dm\textsuperscript{3} s\textsuperscript{-1} was given for the dimerization rate constant [reaction (1)]. A more accurate simulation of the cyclic voltammogram, taking account of the large double layer charging current, and of the exact value of the potential where the scan is reverted not far

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{voltammogram.png}
\caption{Cyclic voltammetry of CO\textsubscript{2} (1.36 mmol dm\textsuperscript{-3}) in DMF (+0.1 mol dm\textsuperscript{-3} Bu\textsubscript{4}NClO\textsubscript{4}) at a mercury electrode. Scan rate: 0.1 V s\textsuperscript{-1} Temp.: 25°C.}
\end{figure}
from the foot of the cathodic, gives a value of $5 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The number of electrons per molecule is close to 1 when $[\text{CO}_2] > 5 \text{ mmol dm}^{-3}$, a stoichiometry that agrees with the formation of oxalate as well as the formation of CO (and carbonate). The number of electrons per molecule increases, 'plateauing' at a value of 2, upon decreasing the CO$_2$ concentration. The change in the electron stoichiometry is most likely related to the increasing interference of CO$_2$$^{2-}$ protonation by residual water [reaction (4)] and of the ensuing electron transfer reactions (5) and/or (5').

Upon raising the concentration of CO$_2$ to the saturation value (0.231 mol dm$^{-3}$), the shape of the voltammogram remains unchanged and the peak current is proportional to concentration (Fig. 2) provided that the ohmic drop is carefully compensated for by means of a positive feedback device.$^{35}$ The shape of the voltammograms indicates that the current is jointly governed by diffusion and by the irreversible kinetics of the initial electron uptake.$^{35}$

These conclusions are at variance with those of an earlier investigation of the reaction in acetonitrile at a low scan rate (20 mV)\textsuperscript{27} log(current) vs. potential plots (Tafel plots) exhibit two successive straight lines of different slopes that were assigned to two successive electrode reactions. We suspect non-compensated ohmic drop to be responsible for this behaviour as illustrated in Fig. 3 where Tafel plots obtained in the same solvent, at the same scan rate, with and without compensation of the ohmic drop are shown. Because the scan rate is low, the diffusion of species to and from the electrode is not semi-infinite but takes place within a steady-state diffusion layer arising from natural convection (see ref. 36 and references therein). The consequence is that the voltammograms, unlike those obtained at higher scan rates (Fig. 1 and 2), are plateau-shaped (as rotating disk electrode voltammograms) rather than peak-shaped. When ohmic drop is correctly compensated for, the Tafel transformation of the voltammogram exhibits first a linear section with a $1/95 \text{ mV}$ slope where the current, $i$, representative of mass transport (diffusion + convection) of CO$_2$ towards the surface. In the absence of ohmic drop compensation, the increasing interference of ohmic drop delays the appearance of mass transport control. As the potential becomes more and more negative, the increase in the reduction current is increasingly compensated for by a parallel increase in the ohmic drop, thus decreasing the slope of the $\log i$ vs. $E$ plot before the limiting current, $i_L$, is eventually reached. Under such conditions, the Tafel plot is well simulated by the equation, $-2.21 - R_i - 0.095 \log i + 0.095 \log(i - i_L)$ ($E$ in V vs. SCE, $I$ in A) where $R = 140 \Omega$, and $i_L = 2.95$ as seen in Fig. 3, where we have also shown how such a Tafel plot can be convolved with two successive straight lines, giving the impression of two successive electrode reactions.

Since the current–potential responses are governed by diffusion and by the irreversible kinetics of the initial electron transfer, cyclic voltammetry, as with any other non-destructive interrogation of the reaction, provides scarce information on the follow-up steps, particularly on the competition between the pathways that lead from the initial radical anion to the final products (Scheme 1).

Analysis of the product distribution upon preparative-scale electrolysis was then necessary to get additional mechanistic information. In order to simplify the problem we have reduced the water content of the solvent down to levels (see Experimental section) where the production of formate is negligible. Most experiments were carried out at mercury, taken as a prototype of a presumably inert electrode at a low current density (1.6 mA cm$^{-2}$). The product distributions obtained at 25°C and at lower temperatures are listed in Table 1. One

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure3.png}
\caption{Tafel plots for the reduction of CO$_2$ in CH$_3$CN (+0.1 mol dm$^{-3}$ Et$_4$NClO$_4$) at a mercury electrode. Temp.: 25°C. CO$_2$ conc. 0.2 mol dm$^{-3}$. Scan rate: 0.02 V s$^{-1}$. Dotted line: with positive feedback compensation of the ohmic drop; full line: without compensation. The open circles represent the fitting of the Tafel plot for the uncompensated current-potential curve with the equation $-2.21 - R_i - 0.095 \log i + 0.095 \log(i - i_L)$; $R = 140 \Omega$, $\log i_L = 2.95$.}
\end{figure}

\begin{table}[h]
\centering
\caption{Variation of product distribution with temperature in direct electrochemical constant current reduction of CO$_2$ in DMF (+0.2 mol dm$^{-3}$ Bu$_4$NClO$_4$) at a mercury electrode$^a$}
\begin{tabular}{c|ccc|c}
\hline
\textbf{temperature (°C)} & \textbf{[CO$_2$]} /mmol dm$^{-3}$ & \textbf{CO$_2$O$_2$$^{2-}$} (%) & \textbf{CO} (%) & \textbf{$R_{CO}^{a}$} & \textbf{$R_{CO2}^{a,b}$} \\
\hline
25 & 152 & 67 & 25 & 0.27 & 0.73 \\
 & 102 & 57 & 40 & 0.20 & 0.80 \\
35 & 199 & 1.4 & 82 & 0.98 & 0.02 \\
 & 101 & 3.5 & 91 & 0.96 & 0.04 \\
45 & 152 & 43 & 49 & 0.53 & 0.47 \\
 & 102 & 56 & 33 & 0.37 & 0.63 \\
60 & 152 & 33 & 64 & 0.66 & 0.34 \\
 & 102 & 42 & 48 & 0.54 & 0.46 \\
 & 102 & 23 & 75 & 0.77 & 0.23 \\
 & 102 & 23 & 69 & 0.75 & 0.25 \\
 & 102 & 23 & 69 & 0.75 & 0.25 \\
 & 102 & 19 & 77 & 0.80 & 0.20 \\
\hline
\end{tabular}
\footnotesize{$^a$ Unless otherwise stated. $^b$ With respect to the total quantity of electricity consumed. $^c R_{CO} = \text{CO yield} / [\text{CO}]/[\text{CO}_2] + [\text{CO}_2O_2^{2-}]$; CO yield with respect to the total quantity of CO and oxalate. $^d R_{CO2} = [\text{CO}_2O_2^{2-}]/[\text{CO}]/[\text{CO}_2] + [\text{CO}_2O_2^{2-}]$; oxalate yield with respect to the total quantity of CO and oxalate. $^e$ Gold. $^f$ Platinum.}
\end{table}
is not very fast.

Under these conditions, the competition parameter, $k_3/k_2$, of reaction (2) is not thermodynamically very favourable.

The rate constants of reaction (0) and (2) can be derived from the product distribution data at 25°C (Table 2), and observed steady increase in the CO yield with CO$_2$ concentration.

Discussion

One of the most striking features of the product distribution obtained from homogeneous catalysis by aromatic ester and nitrile radical anions is the almost total absence of CO formation as opposed to direct electrolysis where CO and oxalate are formed in variable amounts according to the CO$_2$ concentration and temperature. It is also worth noting that at platinum and gold electrodes (which are metals known to adsorb CO) CO is the only electrolysis product (Table 1). The mechanism of homogeneous catalysis by aromatic ester and nitrile radical anions is as depicted in Scheme 2, where P and Q represent the oxidized and reduced forms of the catalyst couple, respectively. The rate constants of reaction (0) were determined in an extended series of aromatic ester and nitrile catalysts. The product distribution was rationalized by the fact that, in its competition with the dimerization step to the CO$_2$/CO$_2^-$ couple, is $0.07 \text{ mol}^{-1} \text{ dm}^3$ and $5 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively. However, except for the initial electron transfer step, such a mechanism is similar to the mechanism of the homogeneously catalysed reduction discussed earlier (Scheme 2), although the second electron transfer step involves the CO$_2^-$ radical anion instead of the radical anion of the catalyst. Qualitatively, it seems unlikely therefore that the reaction sequence in Scheme 1 should lead to the formation of significant amounts of CO, while the set of reactions in Scheme 2 leads exclusively to oxalate. The problem can be put in quantitative terms as follows. For the disproportionation mechanism depicted in Scheme 1, the product selection parameter is $\rho_{\text{disp}} = (K_3/k_2/k_1)_{[CO_2]}$ and the yields of CO and oxalate are given by:

$$y_{\text{CO}} = 1 - y_{\text{oxalate}} = \rho_{\text{disp}}/(1 + \rho_{\text{disp}})$$

Fig. 4 shows an attempt to fit the product distribution data at 0°C (Table 2) with the theoretical predictions for the disproportionation mechanism. It is seen that the fit is not satisfactory, the experimental variation of the CO yield with the CO$_2$ concentration being significantly steeper than predicted by the theoretical curve. This is a first indication against the mechanism depicted in Scheme 1. Another, more direct argument can be derived from the product distribution data at 25°C (Table 1). Previously estimated values of $K_2$ and $k_1$ at 25°C are 0.07 mol$^{-1}$ dm$^3$ and $5 \times 10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$, respectively. The value of $k_3$ for a potential of -2.21 V vs. SCE, corresponding to the CO$_2$/CO$_2^-$ couple, is $10^4$ mol$^{-1}$ dm$^3$ s$^{-1}$ and thus $k_3 \approx 10^6$ mol$^{-1}$ dm$^3$ s$^{-1}$. Under these conditions, log $\rho_{\text{disp}} = -3.8$ for the largest concentration of CO$_2$ (0.152 mol dm$^{-3}$).

**Table 2** Variation of product distribution with concentration in direct electrochemical constant current reduction of CO$_2$ in DMF (+0.2 mol dm$^{-3}$ Bu$_4$NClO$_4$) at a mercury electrode at 0°C

<table>
<thead>
<tr>
<th>[CO$_2$] /mol dm$^{-3}$</th>
<th>CO$_2^-$ (%)</th>
<th>CO (%)</th>
<th>$R_{\text{CO}}$</th>
<th>$R_{\text{CO}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>89</td>
<td>10</td>
<td>0.10</td>
<td>0.90</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>12</td>
<td>0.13</td>
<td>0.87</td>
</tr>
<tr>
<td>42</td>
<td>74</td>
<td>26</td>
<td>0.26</td>
<td>0.74</td>
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<tr>
<td>55</td>
<td>66</td>
<td>34</td>
<td>0.34</td>
<td>0.66</td>
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<tr>
<td>75</td>
<td>49</td>
<td>46</td>
<td>0.48</td>
<td>0.52</td>
</tr>
<tr>
<td>102</td>
<td>42</td>
<td>48</td>
<td>0.54</td>
<td>0.46</td>
</tr>
<tr>
<td>125</td>
<td>33</td>
<td>64</td>
<td>0.66</td>
<td>0.44</td>
</tr>
<tr>
<td>217</td>
<td>23</td>
<td>76</td>
<td>0.77</td>
<td>0.23</td>
</tr>
</tbody>
</table>

*With respect to the total quantity of electricity consumed. $R_{\text{CO}} = \text{CO(%)}/[\text{CO(%) + CO}_2^-]$: CO yield with respect to the total quantity of CO and oxalate. $R_{\text{CO}_2} = [\text{CO(%) + CO}_2^-]/[\text{CO(%) + CO}_2^-]$: oxalate yield with respect to the total quantity of CO and oxalate.

notes a steady increase of the CO yield, and a converse decrease of the oxalate yield, upon decreasing temperature. From the results in Table 1 where, at each temperature, the product distribution was determined for two concentrations, it is already apparent that the yield in CO decreases (and conversely, the oxalate yield increases) as the CO$_2$ concentration decreases. We have investigated this concentration dependence in more detail at 0°C, as reported in Table 2, and observed steady increase in the CO yield with CO$_2$ concentration.
meaning that the formation of CO is predicted to be negligible while the experimental yield is 25% (Table 1).

We must therefore envisage another mechanism possibility for the mechanism of the direct electrochemical reduction, namely the possibility of an 'ECE' mechanism, i.e. that the reduction of the CO₂⁻CO₃⁻⁻ adduct would occur according to reaction (3) instead of reaction (3') in Scheme 1. However, at the low current density employed in this work (1.6 mA cm⁻²), the electrolysis potential is located at ~-2.08 V vs. SCE [from the current-potential curve in Fig. 2(a)], i.e. slightly positive to the standard potential of the CO₂⁻CO₃⁻⁻ couple and the standard potentials of benzonitrile and methylbenzoate. For this reason we do not expect the competition to be more in favour of CO formation in this case than it is in redox-catalysed electrolysis and than it is predicted to be for the direct electrolysis 'DISP' mechanism discussed above. It follows that the characteristics of the steps in the ECE version of Scheme 1 particularly those of step (2) should be influenced by the proximity of the electrode surface. However, in the case of a mercury electrode, specific chemical interaction with the electrode material is unlikely for the following reasons. As discussed earlier, previous observation of a two-phase Tafel plot is not an indication of significant adsorption of the reactants or intermediates but merely results from an ohmic drop effect. At mercury and lead electrodes, the reduction takes place at potentials close to the standard potential of the CO₂⁻CO₃⁻⁻ couple and gives rise to closely similar current-potential curves. The same is true for the current-potential curves obtained upon photoinjection of electrons and capture by CO₂⁻. For the same current density and CO₂⁻ concentration, the product distribution is the same with both electrodes. These observations point to the lack of chemical involvement of the electrode material in the reaction.

We thus propose that the formation of the CO₂⁻CO₃⁻⁻ adduct takes place at the electrode surface near the reaction site where the CO₂⁻ radical is generated and that the ensuing steps occur as represented in Scheme 3 where the dotted line represents the potential profile from the electrode surface to the outer Helmholtz plane (OHP, where the centres of charge of the bulky tetrabutylammonium cations of the supporting electrolyte are located) and from the OHP to the solution. The polarizable CO₂⁻ radical anion interacts electrostatically with the negative charges on the electrode surface and, at their other end, with the tetrabutylammonium cations. This effect helps to enhance their reactivity toward the CO₂ molecules present at the electrode surface. The Lewis acidity of the latter is also likely to be enhanced by the electric field (similar to the enhancement in the acidity of Brønsted acids). Thus it is likely that these two effects make the formation of the CO₂⁻CO₃⁻⁻ adduct [reaction (2)] more favourable than in the solution (the equilibrium constant is denoted K₁). We assume that the rate-determining step in the CO formation path at the electrode surface is reaction (3) (with a surface rate constant k₂), reaction (2) acting as a pre-equilibrium. Following the representation of the reaction mechanism in Scheme 3, the current density, I, is composed of two contributions, I₁ and I₂, representing the reduction of CO₂ and of the CO₂⁻CO₃⁻⁻ adduct respectively (I = I₁ + I₂). Since, as discussed earlier, the current density is small compared with the plateau current density for the reduction of CO₂, we may assume that the CO₂ concentration is constant and equal to its bulk value throughout the system. At the electrode surface:

\[
\frac{I_1}{F} = K_1^2 K_2^3 [\text{CO}_2][\text{CO}_2^{2-}]_{\text{OHP}} - D \frac{d[\text{CO}_2^{2-}]}{dx} \quad 0
\]

\[
\frac{I_2}{F} = K_1^2 K_2^3 [\text{CO}_2][\text{CO}_2^{2-}]_{\text{OHP}}
\]

where the subscript 0 stands for the plane in between the diffuse double layer and the diffusion-reaction layer. As results from the foregoing discussion, the oxalate formation path overruns the CO formation path in the diffusion-reaction layer:

\[
d^2[\text{CO}_2^{2-}] \overline{dx^2} = 2k_1[\text{CO}_2^{2-}]^2
\]

Since the dimerization [reaction (1)] is fast, the CO₂⁻ profile decreases to zero within a reaction layer which is thin compared with the diffusion layer. CO is formed exclusively by surface reactions as shown in Scheme 3. The yields of CO and oxalate are obtained from the following equation.

\[
y\text{CO} = 1 - y\text{oxalate} = \frac{I_2}{I_1}
\]

Combination of these various equations leads to:

\[
y\text{CO} \left[ 1 + \frac{4}{3\rho_{\text{PCE}}} \left( \frac{y\text{CO}}{1 + y\text{CO}} \right)^{1/2} \right] = 1
\]

after introduction of the product selection governing parameter,

\[
\rho_{\text{PCE}} = \frac{K_1^2 K_2^3 [\text{CO}_2]}{(k_1 I_D/P)^{1/3}}
\]

As seen in Fig. 5, there is excellent agreement between the predicted and experimental variations of the CO yield with CO₂ concentration (from Table 2) which corresponds to \(K_1^2 K_2^3 k_1 I_D/P = 8 \text{ dm}^6 \text{ mol}^{-1} \text{ s}^{-1}\) and thus \(K_1^2 K_2^3 = 0.56 \text{ dm}^6 \text{ mol}^{-1} \text{ s}^{-1}\) (\(K_1^2\) has no dimensions, \(K_2^3\) is in dm⁶ mol⁻¹ s⁻¹ as for any surface reaction). It is also interesting to examine the variations of the yields with temperature (Table 1) in the light of the above model. In the Arrhenius plot shown in Fig. 6, the working curve in Fig. 5 has been used to derive the value of the rate parameter from the product distribution data of Table 2. It is seen that the rate parameter in Fig. 6 increases when the temperature decreases corresponding to an overall exothermic process with an enthalpy of 7.6 kcal mol⁻¹. There is little doubt that this variation is mainly due to the fact that equilibrium (2) is an exothermic reaction thanks to the electrostatic interactions that decrease in standard free energy and to the fact that it has a negative entropy.

**Conclusion**

There is a striking difference between direct electrolysis of CO₂ in DMF at an inert electrode, such as mercury, which
produces mixtures of CO and oxalate, and electrolysis catalyzed by radical anions of aromatic esters and nitriles which produces exclusively oxalate in the same medium. Examination of previous results concerning direct electrochemical reduction and reduction by photoinjected electrons reveals that there is no significant specific interactions between reactants, intermediates, products and the electrode material when this is Hg or Pb. From these observations, and from a systematic study of the variations of the oxalate and CO yields with temperature and CO$_2$ concentration, a consistent mechanistic model of the direct electrochemical reduction may be proposed. It involves the formation of oxalate from the coupling of two CO$_2$ radical anions in solution. CO (and an equimolar amount of carbonate) is produced by reduction at the electrode of a CO$_2$-CO$_3^{2-}$ adduct, the formation of which at the electrode surface is made exothermic by non-specific electrostatic interactions.

Fig. 5 Fitting of the direct electrolysis data of Table 2 (●) with the surface ECE mechanism (solid line)

Fig. 6 Arrhenius plot derived from the data of Table 2 by means of the surface ECE model in Scheme 3

References


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