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

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Direct electrolysis of CO\(_2\) 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 CO\(_2\) 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 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\(_2\)\(^{--}\) 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 CO\(_2\) radical anion requires a fairly negative potential (the standard potential of the CO\(_2\)/CO\(_2\)\(^{--}\) couple in \(N,N’\)-dimethylformamide (DMF) with 0.1 mol dm\(^{-3}\) NEt\(_3\)ClO\(_4\) 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 both 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 CO\(_2\)/CO\(_2\)\(^{--}\) 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.\(^3\)\(^4\) The relative amounts of oxalate and carbon monoxide depend upon current density and CO\(_2\) concentration, and the presence of water promotes the formation of formate.\(^2\) Other metals presumably play a catalytic role through chemisorption of CO\(_2\), intermediates or products. CO\(_2\) 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 ago\(^6\) and confirmed by more recent studies.\(^7\) 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 CO\(_2\)\(^{--}\) other products such as formaldehyde,\(^1\)\(^2\) methanol\(^1\)\(^3\)\(^4\) and methane\(^1\)\(^5\)\(^6\)\(^7\)\(^8\) 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,\(^9\) 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 CO\(_2\) concentration suggested the mechanism depicted in Scheme 1.\(^1\)\(^2\)\(^3\)\(^4\)\(^7\) Oxalate is considered to be formed from the coupling of two CO\(_2\) radical anions [reaction (1)] while the production of CO, and of an equimolar amount of carbonate, involves, as intermediate, an adduct between CO\(_2\) and its radical anion where the C--O bond formed results from the donation of an electron pair from carbonate, 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 CO and carbonate [reactions (3) and (3’)]. The formation of formate involves the water that is present which may protonate CO\(_2\)\(^{--}\) leading to a neutral radical [reaction (4)]

\[
\text{(0) } \text{CO}_2 + e^- \rightarrow \text{CO}_2^{-} \\
\text{(1) } 2 \text{CO}_2^{-} \rightarrow \text{O}^- + \text{C} = \text{O}^- \\
\text{(2) } \text{CO}_2^{-} + \text{CO}_2 \rightarrow \text{O}^- + \text{CO}_2^- \\
\text{(3) } \text{O}^- + \text{e}^- \rightarrow \text{CO} + \text{CO}_2^- \\
\text{(3') } \text{O}^- + \text{CO}_2^- \rightarrow \text{CO} + \text{CO}_2^- + \text{CO}_2 \\
\text{(4) } \text{CO}_2^- + \text{H}_2\text{O} \rightarrow \text{HCO}_2^- + \text{OH}^- \\
\text{(5) } \text{HCO}_2^- + e^- \rightarrow \text{HCO}_2^- \\
\text{(5') } \text{HCO}_2^- + \text{CO}_2^- \rightarrow \text{HCO}_2^- + \text{CO}_2 \\
\text{Scheme 1}
\]

from which formate is derived after an additional electron transfer step [reactions (5) and (9)]. It has been found recently that radical anions of aromatic esters and nitriles may be used to catalyse homogeneously the electrochemical reduction of CO\(_2\). 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\(_2\) at inert electrodes. For this reason we analysed in a more systematic manner the effect of CO\(_2\) concentration on product distribution. We also investigated the effect of temperature. The discussion will take into account the content, based on Tafel plots and photoemission experiments, that specific adsorption is an essential factor of the reduction mechanism, even for electrodes previously prepared inert such as mercury and lead, in water\(^{26}\) as well as in aprotic solvents.\(^{27}\) 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\(_2\)CO\(_3\) for several days and stirred occasionally. It was then fractionally distilled under reduced pressure under N\(_2\) twice and stored in a dark bottle under N\(_2\). In order to remove as much residual water as possible the solvent was repetitively percolated before use through a column of neutral alumina (Merck, activity grade 1) previously activated overnight at 360°C under vacuum. Tetrabutylammonium perchlorate (Fluka purum) was recrystallized twice from a 2:1 water–ethanol mixture and then dried in a vacuum oven at 60°C. CO\(_2\) (99.998%) was supplied by SIAD (Italy). The solubility of the gas in DMF (0.199 mol dm\(^{-3}\) at 25°C and 1 atm pressure) at various temperatures and various partial pressures has been reported previously.\(^{28}\) DMF solutions containing various concentrations of CO\(_2\) were prepared by saturating the solvent with appropriate mixtures of CO\(_2\) and argon. The apparatus used for the preparation of the gas mixtures and the method of calculating CO\(_2\) concentrations in the solution from its partial pressure in the gas phase have been described previously.\(^{28}\)

**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,\(^{29}\) 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 IFELEC 2502 chart recorder were used for recording the cyclic voltammograms. A mercury micro-electrode was used as working electrode and a recorder were used for recording the cyclic voltammograms. Aminex HPX-87H ion-exchange column eluted with 0.005 mol dm\(^{-3}\) H\(_3\)PO\(_4\) Supelco column. Oxalate was directly analysed in HPLC with a Perkin Elmer Series 4 liquid chromatograph equipped with a UV detector operating at 210 nm, using an Aminex HPX-87H ion-exchange column eluted with 0.005 mol dm\(^{-3}\) H\(_2\)SO\(_4\) on which conversion of oxalate to oxalic acid takes place. The validity of this procedure was checked by comparison with the classical permanganate colorimetric method.\(^{34}\)

**Results**

Fig. 1 shows a typical cyclic voltammogram of CO\(_2\) in DMF. The cathodic peak remains irreversible up to 1000 V s\(^{-1}\). 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\(^{-1}\)) from which an approximate estimate of the standard potential of the CO\(_2\)/CO\(_2\)\(^{-}\) couple (−2.21 V vs. SCE) in DMF +0.1 mol dm\(^{-3}\) Bu\(_4\)NCIO\(_4\)) was derived.\(^{28}\) In the original publication, a rough estimate of 10\(^{7}\) mol dm\(^{-3}\) s\(^{-1}\) 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

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**Fig. 1** Cyclic voltammetry of CO\(_2\) (1.36 mmol dm\(^{-3}\)) in DMF (+0.1 mol dm\(^{-3}\) Bu\(_4\)NCIO\(_4\)) at a mercury electrode. Scan rate: 0.1 V s\(^{-1}\) Temp.: 25°C.

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from the foot of the cathodic, gives a value of $5 \times 10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$. The number of electrons per molecule is close to 1 when [CO$_2$] > 5 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$$^-$ 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. The shape of the voltammograms indicates that the current is jointly governed by diffusion and by the irreversible kinetics of the initial electron uptake.

These conclusions are at variance with those of an earlier investigation of the reaction in acetonitrile at a low scan rate (20 mV)$^{-1}$. 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. 56 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 $1/95$ mV slope where the peak, the current plateaus at a value, $i_p$, representative of mass transport (diffusion + convection) of CO$_2$ toward 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, $-2.21 - R_i - 0.095 \log i + 0.095 \log i_l - i_l$ (E vs. SCE, $i$ in A) where $R = 140 \Omega$, and log $i_l = -2.95$ as seen in Fig. 3, where we have also shown how such a Tafel plot can be con-
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$_2$] /mmol dm$^{-3}$</th>
<th>C$_2$O$_4^{2-}$ (%)</th>
<th>CO (%)</th>
<th>$R_{CO}$</th>
<th>$R_{CO,oxalate}^{i}$</th>
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<tr>
<td>20</td>
<td>89</td>
<td>10</td>
<td>0.10</td>
<td>0.90</td>
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<td>30</td>
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<td>0.87</td>
</tr>
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<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>
</tr>
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<td>0.52</td>
</tr>
<tr>
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<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. $R_{CO} = \text{CO}(%)/[\text{CO}(%)]$; the CO yield with respect to the total quantity of CO and oxalate.

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 $k_5$ and $k_4$ at 25°C are 0.07 mol$^{-1}$ dm$^3$ and 5 x 10$^3$ mol$^{-1}$ dm$^3$ s$^{-1}$, respectively. The value of $k_5$ for a potential of -2.21 V vs. SCE, corresponding to the CO$_2$/CO$_2$ radical anion, is 10$^4$ mol$^{-1}$ dm$^3$ s$^{-1}$ and thus $k_5 \approx 10^6$ 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$^{-3}$).

**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 the 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 mechanistic possibility for the CO formation is 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 $k_5$ and $k_4$ at 25°C are 0.07 mol$^{-1}$ dm$^3$ and 5 x 10$^3$ mol$^{-1}$ dm$^3$ s$^{-1}$, respectively. The value of $k_5$ for a potential of -2.21 V vs. SCE, corresponding to the CO$_2$/CO$_2$ radical anion, is 10$^4$ mol$^{-1}$ dm$^3$ s$^{-1}$ and thus $k_5 \approx 10^6$ 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$^{-3}$).

Reactions depicted in Scheme 1 are less favourable thermodynamically than reaction (2) because the formation of CO$_2$ as opposed to direct electrolysis where CO and oxalate are formed (Table 1). Previously estimated values of $k_5$ and $k_4$ at 25°C are 0.07 mol$^{-1}$ dm$^3$ and 5 x 10$^3$ mol$^{-1}$ dm$^3$ s$^{-1}$, respectively. The value of $k_5$ for a potential of -2.21 V vs. SCE, corresponding to the CO$_2$/CO$_2$ radical anion, is 10$^4$ mol$^{-1}$ dm$^3$ s$^{-1}$ and thus $k_5 \approx 10^6$ 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$^{-3}$).

Why is product distribution in direct electrolyses much more in favour of the formation of carbon monoxide than in homogeneous catalysis? What are the reasons for the observed variations of product distribution in direct electrolyses with CO$_2$ concentration and temperature (Tables 1 and 2)?

Previous preparative-scale studies in DMF at mercury and lead electrodes also revealed the formation of both oxalate and CO$_2$. They have been rationalized in the framework of the mechanism depicted in Scheme 1 where the dimerization and adduct formation steps following first electron transfer were assumed to occur homogeneously. 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 $\rho_{\text{disp}}^{i} = (K_5 k_4/1)^{1/2} [\text{CO}_2]^{1/4}(1/F D^{1/2})^{1/2}$ and the yields of CO and oxalate are given by:

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

($y_{\text{CO}}$ = CO yield, $y_{\text{oxalate}}$ = oxalate yield, $\rho_{\text{disp}}^{i} = (K_5 k_4/1)^{1/2} [\text{CO}_2]^{1/4}(1/F D^{1/2})^{1/2}$)

**Scheme 2**

$$p + e^- \rightarrow Q$$

(0)

$$2\text{CO}_2' \rightarrow \text{CO} + \text{CO}_2' + \text{P}$$

(1)

$$\text{CO}_2' + \text{CO}_2 \rightarrow \text{CO}_2^2^- + \text{P}$$

(2)

$$\text{Q} + \text{CO} + \text{CO}_2^2^- + \text{P}$$

(3)
meaning that the formation of CO is predicted to be negligible while the experimental yield is 25% (Table 1).

We must therefore envisage another mechanistic possibility for the mechanism of the direct electrochemical reduction, namely the possibility of an 'ECE' mechanism, i.e. that the reduction of the CO$_2$/CO$_2^-$ 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 CO$_2$/CO$_2^-$ 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 electrolys '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 CO$_2$/CO$_2^-$ 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 CO$_2$.

For the same current density and CO$_2$ 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 CO$_2$-CO$_2^-$ adduct takes place at the electrode surface near the reaction site where the CO$_2^-$ 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 CO$_2^-$ 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 CO$_2$ 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 CO$_2$-CO$_2^-$ adduct [reaction (2)] more favourable than in the solution (the equilibrium constant is denoted $K^S$). We assume that the rate-determining step in the CO$_2$ formation path at the electrode surface is reaction (3) with a surface rate constant $k_3$, 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, $I_1$ and $I_2$, representing the reduction of CO$_2$ and of the CO$_2$-CO$_2^-$ adduct respectively ($I = I_1 + I_2$). Since, as discussed earlier, the current density is small compared with the plateau current density for the reduction of CO$_2$, we may assume that the CO$_2$ concentration is constant and equal to its bulk value throughout the system. At the electrode surface:

$$I_1 = K^S K_3 x_0 [CO_2][CO_2^-]_0$$

$$I_2 = K^S K_3 x_0 [CO_2][CO_2^-]_0$$

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:

$$d^2[CO_2^-]_0 = 2k_1[CO_2^-]^2$$

Since the dimerization reaction (1) is fast, the CO$_2^-$ 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:

$$y^{CO} = 1 - y^{oxalate} = \frac{I_2}{I_1}$$

Combination of these various equations leads to:

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

after introduction of the product selection governing parameter,

$$\rho_{PCE} = \frac{K^S K_3 x_0 [CO_2]}{(k_1 I D/F)^{1/3}}$$

As seen in Fig. 5, there is excellent agreement between the predicted and experimental variations of the CO yield with CO$_2$ concentration (from Table 2) which corresponds to $K^S K_3 x_0 (k_1 I D/F)^{1/3} = 8$ dm$^6$ mol$^{-1}$ and thus $K^S K_3 x_0 = 0.56$ dm$^6$ mol$^{-1}$ s$^{-1}$ (K$^S$ has no dimensions, $K_3$ is in dm$^6$ mol$^{-1}$, $k_1$ in dm$^3$ 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 CO$_2$ in DMF at an inert electrode, such as mercury, which

produces mixtures of CO and oxalate, and electrolysis catalysed 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 CO₂ concentration, a consistent mechanistic model of the direct electrochemical reduction may be proposed. 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 made exothermic by non-specific electrostatic interactions.