Electrocatalytic Reduction of Carbon Dioxide to Methanol. Part 5.[1] Relationship between the Ability of Metal Complexes to engage in Homogeneous Catalysis and their Co-ordination Chemistry

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Carbon dioxide has been reduced to methanol at a mediated electrode in the presence of a metal complex and a primary alcohol. It has been shown that the ability of the metal complex to engage in the homogeneous catalysis is closely related to its co-ordination chemistry in aqueous solution. The ability of the most highly co-ordinated complex was very low, and unstable as well, as aqua complexes had no catalytic activity. The highest activity was observed with the 1 : 1 form of a metal–bidentate ligand complex. The active site for the reduction reaction of CO_2 was suggested to be a vacancy in the co-ordination shell.

It has been established that carbon dioxide is converted to methanol at room temperature.[2,3] This process involves mediated electron transfer *via* a surface-confined metal complex, *i.e.*, the reduction of CO_2 is caused by the oxidation of the surface-confined metal complex. Various sources of electrons, such as commercial electric power,[2,3] an electrochemical photocell,[1] and a solar cell,[4] have been used in order to regenerate the catalytic activity of the surface-confined complex. It is shown that the continuous reduction of CO_2 can be obtained with a relatively high current efficiency irrelevant to the source of electrons. In this process, however, the existence of homogeneous catalysts consisting of a metal complex and a primary alcohol is prerequisite. The ability of the metal complexes to engage in the homogeneous catalysis depends rather on their characteristics. In the present work, special attention was devoted to the nature of the metal complex operating as the homogeneous catalyst.

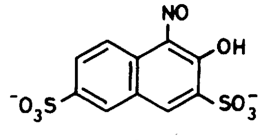
Experimental

The metal complexes used were prepared by dissolving various metal salts and 2-hydroxy-1-nitrosonaphthalene-3,6-disulphonate (L^1) or 4,5-dihydroxybenzene-1,3-disulphonate (L^2) in 0.1 mol dm^{-3} KCl. All metal ions were prepared by dissolving their sulphates.

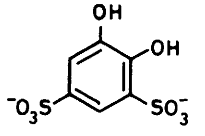
L^1 and L^2 are typical bidentate ligands, and form 1 : 1, 1 : 2, or 1 : 3 complexes with a metal ion. The catalyst solutions consisted of these metal complexes and a primary alcohol (methanol was chiefly used) in 0.1 mol dm^{-3} KCl, and were kept in a reservoir (1 dm^3) through which CO_2 was bubbled at a flow rate of 200 cm^3 min^{-1} for 1 h. The carbon dioxide (Iwadani Co.) used was of 99.7% purity, and all chemicals were of reagent grade.

The surface-confined metal complex used was Everitt's salt, $K_2Fe^{II}[Fe^{II}(CN)_6]$, and was prepared by electroreduction of a film of Prussian blue, $KFe^{III}[Fe^{II}(CN)_6]$, deposited on a platinum plate or stainless steel from an aqueous $FeCl_3$–$K_3[Fe(CN)_6]$ solution.[5,6] Both substrates were in the form of a 0.2-mm thick plate with an exposed area of *ca.* 6 cm^2. The average amount of the film of Everitt's salt was about 2.5×10^{-7} mol dm^{-3}.

The electrochemical photocell used to supply electrons comprised n-cadmium sulphide and the surface-confined Everitt's salt working as the photoanode and the cathode, respectively. The preparation and treatment of the n-CdS electrode have been described previously.[7] The electrochemical cell consisted of a cathode and an anode compartment, which were separated by a fine glass frit. The anode compartment was equipped with a flat quartz window to admit the illuminating light. The light source was a 500-W Xe arc lamp. The cathode was the above modified-platinum or -stainless steel electrode, and the anode n-CdS under the illumination of light. The cathode compartment always contained 40 cm^3 of the catalyst solution, and the same volume of the 0.1 mol dm^{-3} KCl solution with a reducing agent saturated with nitrogen gas was set in the anode compartment. The addition of a reducing agent to the anolyte was necessary in order to suppress the photocorrosion of n-CdS, and the complex $[Fe^{II}(edta)]^{2-}$ (H_4edta = ethylenediaminetetra-acetic acid) was chiefly used for this purpose.



L^1



L^2

Methanol was determined by both gas and steam chromatographic methods. A JGC-1000 gas chromatograph equipped with a thermal conductivity detector and a Poropak Q column was employed. The sampling procedure is described elsewhere.[8] An Ohkura model SSC-1 steam chromatograph with steam as the carrier gas, a flame ionization detector, and a Poropak R column was employed.[9] Aqueous samples were used without any pretreatment.

Results

Absorption spectra of the catalyst solutions consisting of the Co^{II} or Fe^{II} complex of L^1 and methanol are shown in Figure 1. The spectral features are similar for solutions with nitrogen and CO_2, but the absorbance shows a tendency to decrease in the presence of CO_2. This fact may suggest an interaction between the central metal and CO_2 although a description of the exact structure of the metal complex–MeOH–CO_2 system is very difficult from these spectra alone. Figure 2 shows the Job plots for the Co^{II} and Zn^{II} complexes of L^1, where x_M is the mole fraction of the metal ion. In these plots the concentrations of the two constituents were varied wherein their sum was kept constant. A sharp break is seen at $x_M = 0.25$ for the Co^{II} complex, and hence the 1 : 3 complex is suggested. In the Zn^{2+}–L^1 system, however, the formation of a stable complex is not indicated. Although the stability constants of metal complexes with L^1 were not available except for Ni^{II} ($\log \beta_1 = 6.9$), it was found from such plots that not Ca^{2+}, VO^{2+}, Mn^{2+}, Cu^{2+}, or

Table 1. Results of methanol concentration, electric charge (Q), initial and final potentials of the mediated cathode, and current efficiency (η_i) obtained with the electrochemical photocell*

Metal ion	Potential (V *vs.* s.c.e.)		Q/C	[Methanol]/ mmol dm^{-3}	η_i/%
	Initial	Final			
Ca^{2+}	−0.056	+0.002	4.050	(−0.006)	
VO^{2+}	+0.204	+0.241	3.567	(−0.013)	
Cr^{3+}	+0.107	+0.117	3.793	(−0.004)	
Fe^{3+}	−0.083	+0.480	3.611	(−0.006)	
Mn^{2+}	−0.078	+0.015	4.493	(−0.021)	
Fe^{2+}	−0.318	−0.313	2.638	0.095	83.4
Co^{2+}	−0.212	−0.188	5.206	0.136	60.5
Ni^{2+}	−0.195	−0.138	4.744	0.053	25.9
Zn^{2+}	−0.115	−0.048	5.010	(−0.013)	

* Volume of the test solution, 40 cm^3; added methanol, 20 mmol dm^{-3}; metal ion, 15 mmol dm^{-3}; L^1, 15 mmol dm^{-3}; pH, 3.5. Substrate of the mediated cathode, platinum; reaction time, 5 h. Anolyte, N_2-saturated 0.1 mol dm^{-3} KCl solution containing 10 mmol dm^{-3} $[Fe^{II}(edta)]^{2-}$.

Table 2. Results of methanol concentration, electric charge, initial and final potentials of the mediated cathode, and current efficiency obtained with the electrochemical photocell[a]

Metal ion	Potential (V *vs.* s.c.e.)		Q/C	[Methanol]/ mmol dm^{-3}	η_i/%
	Initial	Final			
Ca^{2+}	−0.406	−0.401	1.174	(−0.009)	
VO^{2+}	−0.391	−0.368	1.594	0.041	59.6
Cr^{3+}	−0.409	−0.406	1.147	0.041	82.8
Fe^{3+}[b]	−0.268	−0.099	4.101	0.129	72.9
Mn^{2+}	−0.394	−0.387	0.871	(−0.005)	
Fe^{2+}	−0.381	−0.417	1.114	0.056	116.5
Co^{2+}	−0.414	−0.466	1.021	(−0.010)	
Ni^{2+}	−0.400	−0.381	1.105	(−0.008)	
Cu^{2+}	+0.163	+0.172	4.401	(−0.006)	
Zn^{2+}	−0.439	−0.419	0.869	(−0.006)	

[a] Details as in Table 1, except that the ligand used was L^2. [b] The concentration of the Fe^{3+} ion was 6.5 mmol dm^{-3}.

Zn^{2+}, but Cr^{3+}, Fe^{2+}, Co^{2+}, or Ni^{2+} form a stable 1 : 3 complex with this ligand. On the other hand, L^2 forms a stable complex not with Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, or Zn^{2+}, but with VO^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, or Cu^{2+}. As described below, the stability of a metal complex was closely related with its catalytic activity in the reduction process of CO_2 although this is a necessary, but not sufficient, condition for the reduction.

In Table 1, the concentration of methanol produced, the electric charge passed, the initial and final potentials of the mediated cathode, and the current efficiency are shown in the presence of various metal ions with L^1. It is seen that in the catalyst systems leading to the reduction of CO_2 the final potential of the mediated cathode is always negative *vs.* the saturated calomel electrode (s.c.e.), except that in the solution with Zn^{2+}. As shown above, the spectroscopic results indicated that L^1 forms a stable complex with Cr^{3+}. In the solution containing the Cr^{III} complex, the final potential of the cathode was +0.117 V *vs.* s.c.e., and there was no formation of methanol. Hence, the metal complex must be stable and in addition the final potential of the mediated cathode must be negative *vs.* s.c.e. when CO_2 is catalytically reduced to methanol. The only catalyst systems which satisfy these conditions are those complexes of Fe^{II}, Co^{II}, and Ni^{II}.

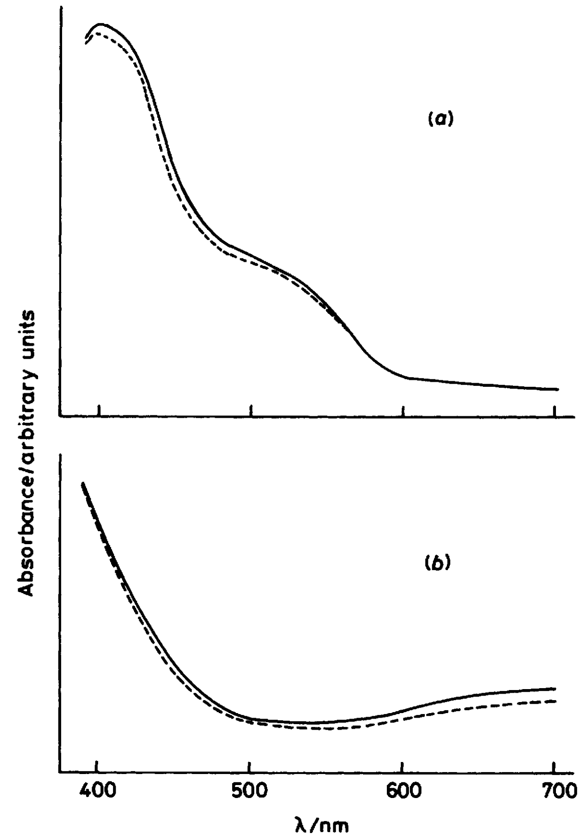


Figure 1. Absorption spectra of catalyst solutions (0.1 mol dm^{-3} KCl, pH 3.5) containing 20 mmol dm^{-3} MeOH with nitrogen (——) or CO_2 (– – – –). (*a*) 15 mmol dm^{-3} Co^{2+} or (*b*) 15 mmol dm^{-3} Fe^{2+} + 15 mmol dm^{-3} L^1

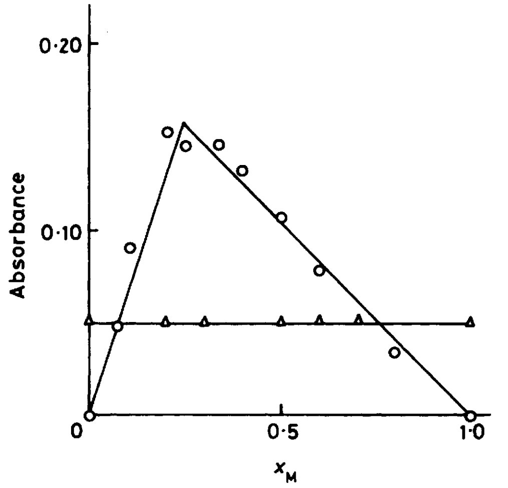


Figure 2. Job plot for Co^{II} and Zn^{II} complexes with L^1: Co^{II} (○) and Zn^{II} (△) at 520 nm. $[Co^{2+}]$ + [ligand] = 0.1 mmol dm^{-3}; $[Zn^{2+}]$ + [ligand] = 0.2 mmol dm^{-3}

Table 2 shows the results obtained in the presence of various metal ions with L^2. The final potentials of the mediated cathode are all negative except that in the solution with Cu^{2+}. The stability constants (log K_1) of M–L^2 complexes are:[10–12] 5.8 (Ca^{2+}), 15.88 (VO^{2+}), 20.7 (Fe^{3+}), 8.6 (Mn^{2+}), 8.2 (Co^{2+}), 9.96 (Ni^{2+}), 12.8 (Cu^{2+}), and 9.0 (Zn^{2+}). The catalyst systems in which the metal complex has log K_1 larger than 12 and where the final potential of the cathode is negative *vs.* s.c.e. can lead to

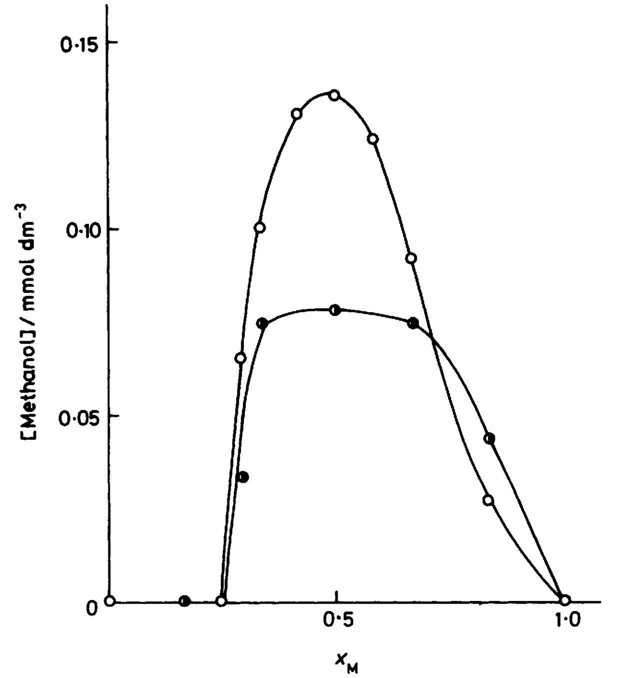


Figure 3. The relationship between the concentration of methanol produced and the mole fraction of Co^{2+}. The sum of the concentrations of Co^{2+} and L^1 was always 30 mmol dm^{-3} and the substrate of the mediated cathode either platinum (○) or stainless steel (◑). The other experimental conditions were the same as those noted in Table 1

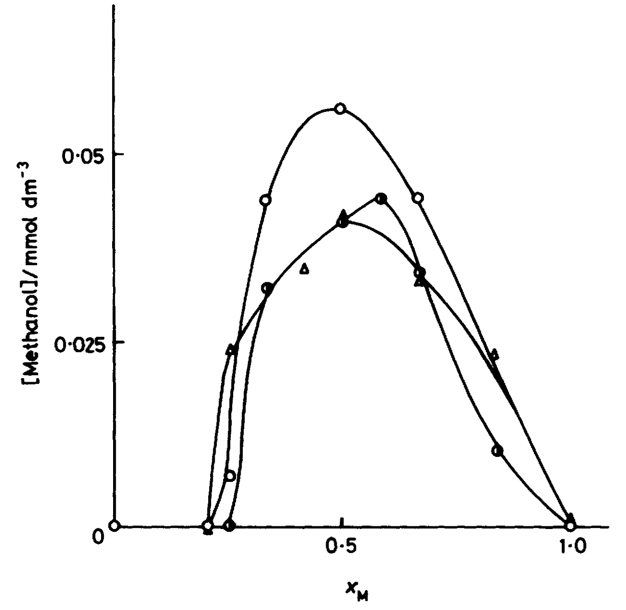
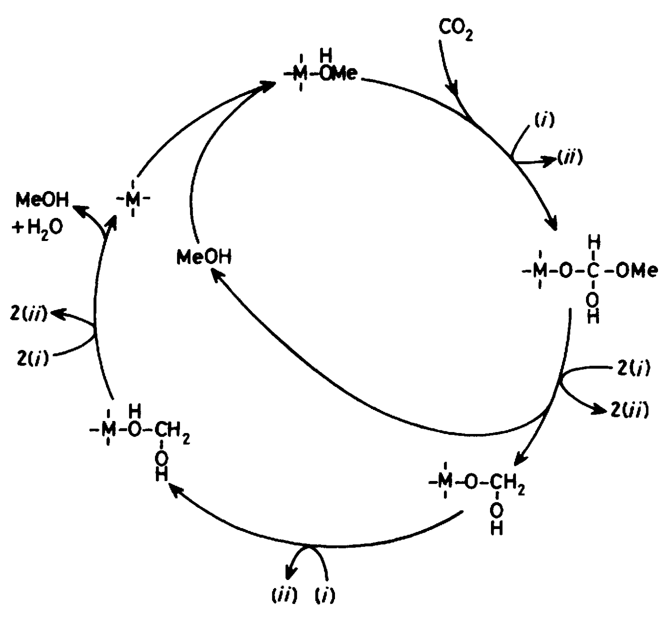


Figure 4. The relationship between the concentration of methanol produced and the mole fraction of the metal. The sum of the concentrations of metal and L^2 was always 30 mmol dm^{-3}. Metal = Fe^{2+} (○), VO^{2+} (◑), or Cr^{3+} (△). The other experimental conditions were the same as those noted in Table 1



Scheme. (*i*) $K_2Fe^{II}[Fe^{II}(CN)_6] + H^+$, (*ii*) $KFe^{III}[Fe^{II}(CN)_6] + K^+$

the formation of methanol. Although the stability constants for the Cr^{III} and Fe^{II} complexes are not available, our Job plots for these complexes with L^2 showed the formation of a stable 1:3 form. Hence this result also indicates that the stability of the metal complex and the electrode potential of the mediated cathode are both critical in the catalytic conversion of CO_2 into methanol.

The concentration of methanol produced is plotted *versus* the mole fraction of metal in Figure 3. At the mediated platinum electrode, the formation of methanol does not occur at $0 < x_M < 0.25$ and $x_M = 1.0$, and it is a maximum at the mole fraction of *ca.* 0.5. This result shows that the metal complex capable of operating as a homogeneous catalyst is in a 1:1 or 1:2 form; in other words, such a complex is neither an aquametal ion nor the most highly co-ordinated species, but has at least one labile ligand (usually water) which is replaced by a new ligand. At the mediated-stainless steel electrode, the maximum concentration of methanol produced is about half that obtained with the mediated-platinum electrode as shown in Figure 3, but the co-ordination chemistry of metal complexes leading to the formation of methanol is the same as that described above.

The plots of the methanol concentration *versus* the mole fraction are shown in Figure 4 for the metal complexes with L^2. The maximum concentrations of methanol produced are observed at the mol fraction of *ca.* 0.5 although the value for VO^{2+} is slightly larger than this value. The minimum mole fraction leading to the formation of methanol, which corresponds to the most highly co-ordinated species, is 0.25 for VO^{2+}, and 0.20 for Fe^{2+} and Cr^{3+}. The deviation of the value from 0.25 may be related to the stability of the metal complex, because in a less stable complex an excess of ligand is necessary when a metal is associated with its maximum number of ligands.

Discussion

The overall reaction for the reduction of CO_2 to methanol is proposed to be as shown in equation (1), and the detailed mechanism as shown in the Scheme.[2]

$$CO_2 + 6H^+ + 6K_2Fe^{II}[Fe^{II}(CN)_6] \rightleftharpoons MeOH + 6KFe^{III}[Fe^{II}(CN)_6] + 6K^+ + H_2O \quad (1)$$

The activation of reaction (1) can only be brought about by homogeneous catalysts consisting of a metal complex and a primary alcohol. In the Scheme a co-ordination bond is first formed between a central metal (M) and a primary alcohol (MeOH); CO_2 inserts into this bond to form a formate-type intermediate, and finally methanol and the initial complex are produced by the reaction with Everitt's salt. In reaction (1), the oxidation of high-spin iron(II) to high-spin iron(III) gives rise to the reduction of CO_2, and in order to obtain the continuous reduction of CO_2 to methanol the re-reduction of iron(III) to iron(II) is required. In the present work, this was achieved with the electrochemical photocell. As shown in Tables 1 and 2, the current efficiency is relatively high. However, the addition of a reducing agent such as $[Fe^{II}(edta)]^{2-}$ to the anolyte was necessary to suppress the photocorrosion of n-CdS in the prolonged electrolysis.

As seen from Tables 1 and 2, the final potential of the mediated-cathode electrode is always negative *vs.* s.c.e. whenever CO_2 is reduced to methanol. Such a low potential is required to re-reduce high-spin iron(III) to high-spin iron(II) in reaction (1). Although the electrode potential at which Prussian blue is reduced to Everitt's salt is *ca.* +0.18 V *vs.* s.c.e.,[5] the final potential obtained here is the mixed potential being determined by the photoanodic and the cathodic processes, and the final potential would remain at the negative side.

In addition to such thermodynamic and kinetic conditions for the formation of methanol, a metal complex acting as the homogeneous catalyst must satisfy a requirement from the co-ordination chemistry. As pointed out above, a metal complex capable of leading to the reduction of CO_2 should have a relatively high stability constant. In catalyst solutions containing an unstable complex, the metal complex decomposed during electrolysis and deposition of the metal was observed on the mediated substrate; *e.g.*, in the solution with Cu^{2+} and L^1, the colourless cathode surface coated with Everitt's salt became yellowish green due to the deposition of copper, and the film of Everitt's salt was completely peeled off after 5 h electrolysis. In the catalyst system consisting of Mn^{2+} and L^1, the major part of the surface film still remained after 5 h electrolysis, but the surface was completely covered with manganese, and Everitt's salt lost its function as the electrode mediator. On the other hand, the most highly co-ordinated complex, *i.e.*, a 1:3 complex of a bidentate ligand, had no catalytic activity since as shown in the Scheme the replacement reaction occurs at the vacancy (really associated with a water molecule) in the co-ordination shell. For a metal complex with a bidentate ligand, the 1:1 complex showed the highest activity.

In the present study, the effect of the substrate of the mediated cathode was shown: the maximum concentration of methanol produced with the stainless steel was about half that obtained with the platinum. The film of Everitt's salt on the stainless steel tended to peel off in prolonged electrolysis, and this tendency was conspicuous in the presence of unstable metal complexes. The absence of Everitt's salt from the substrate, and hence the drop in yield of methanol are probably due to the corrosion of stainless steel followed by the complex formation of the dissolved metal ion with the ligands investigated.

It is therefore concluded that the co-ordination chemistry of a metal complex operating as the homogeneous catalyst as well as the thermodynamic requirement for the electrode potential of the mediated cathode is of importance in the reduction of CO_2.

Acknowledgements

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