Selective Conversion of CO into Methanol at Ordinary Temperature. Part 4.[1] Activation by Iron(II), Iron(III), and Chromium(III) Complexes†

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The conversion of carbon monoxide into methanol has been performed at a platinum electrode modified with $K_2Fe^{II}[Fe^{II}(CN)_6]$. This reaction was activated by catalytic systems consisting of a primary alcohol and a series of iron(II), iron(III), or chromium(III) complexes. The current–time curves at a constant potential showed an oscillation, the period, induction time, and amplitude of which are a function of temperature, applied potential, and the nature and concentration of the metal complex or alcohol added. The pseudo-rate constant, the current efficiency, and the activation energy for the methanol formation have been determined. The current efficiency was almost 100% except in the presence of pentachlorochromate(III) and pentafluoroferrate(II), and the activation energy was 2.9—5.8 kcal mol^{-1}. Infrared spectra of the metal complex isolated from the catalyst solution indicated that the reduction of CO takes place *via* methyl formate as an intermediate. These results are suggestive of a mechanism in which co-ordination of CO to the central metal in the form of methyl formate is a key step, and the diffusion of the co-ordinated species toward the modified electrode is rate determining.

There is currently a resurgence of interest in the Fischer-Tropsch synthesis, oxo–alcohol chemistry, and carbonylation, based on the rise in the price of crude petroleum and the potential of coal as an alternative energy source.[2] The production of methanol or the Fischer-Tropsch process *via* heterogeneous catalysis requires rather extreme operating conditions (200—400 °C and 10—200 atm),[3,4] and a wide variety of by-products is often produced.

The conversion of carbon monoxide into organic chemicals *via* homogeneous catalysis has the following advantages[5,6] over the corresponding heterogeneous process: (*i*) higher selectivity and efficiency for desired products; (*ii*) improved reproducibility and control of the catalyst; (*iii*) resistance to sulphur- and nitrogen-containing poisons; and (*iv*) resistance to carbonization. In general, various transition-metal complexes have been used as catalysts, and the selectivity for the desired products improved to some extent. The process has been studied most thoroughly with metal carbonyl complexes.[7–11] Ruthenium complexes[10] produce methanol together with a small amount of methyl formate, while cobalt complexes[9] give methanol, methyl formate, and cyclohexylmethanol as major products. Although these homogeneous catalyses provide improved selectivity, they still require conditions as extreme as in the heterogeneous system, *e.g.* 200 °C and 300 atm for the cobalt complex. Taking acount of the fact that the reduction of carbon monoxide to methanol is highly favourable thermodynamically, it may be worth investigating whether such severe conditions are really required.[7] The mitigation of rigorous conditions has been of interest to many workers.

To this end, the electrochemical reduction of carbon monoxide has been studied by a few workers. However, hydrogenation by this technique is very difficult. The electroreduction of carbon monoxide was first attempted by Silvestri *et al.*[12,13] The major product obtained in dimethylformamide and at about 200 atm CO is the squarate anion $C_4O_4^{2-}$,[13] while the dimeric anion $C_2O_2^{2-}$ is formed in liquid ammonia and at 14 atm CO.[14] We have developed the conversion of carbon monoxide into methanol at ordinary temperature and atmospheric pressure.[15] This involves an indirect electrochemical process in which carbon monoxide is reduced at Everitt's salt-modified electrode in the presence of hexacyanoferrate(II) and methanol acting as homogeneous catalysts. The conversion reaction has been attempted in the presence of pentachlorochromate(III)[16] or by using a partially immersed electrode.[1] In the present paper a series of iron(II), iron(III), and chromium(III) complexes were employed as homogeneous catalysts, and the general activation process is discussed.

Experimental

The metal complexes used were: aquapentachlorochromate(III), $[NH_4]_2[CrCl_5(H_2O)]$;[17] diaquabis(oxalato)chromate(III), $K[Cr(C_2O_4)_2(H_2O)_2]$;[18] aquapentacyanoferrate(II), $Na_3[Fe(CN)_5(H_2O)]$;[19] aquapentafluoroferrate(III), $K_2[FeF_5(H_2O)]$;[17] amminepentacyanoferrate(II), $Na_3[Fe(CN)_5(NH_3)]$;[20] hexacyanoferrate(II), $K_4[Fe(CN)_6]$;[17] pentacyanonitrosylferrate(III), $Na_2[Fe(CN)_5(NO)]$;[17] and (4,5-dihydroxybenzene-1,3-disulphonato)iron(III), $[Fe^{III}\{C_6H_2(OH)_2(SO_3)_2\}]^+$. These complexes were prepared as described in the literature, except for the last which was formed by dissolving 10^{-3} mol dm^{-3} purified iron(III) sulphate and the ligand (2×10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} KCl. The catalyst solutions comprised these metal complexes and a primary alcohol (MeOH or EtOH) in 0.1 mol dm^{-3} KCl, and the pH was adjusted to 3.5. The yield of methanol produced in the conversion process was much higher with methanol than with ethanol in the catalyst solution, and hence methanol was generally used. The catalyst solutions were kept in a storage vessel (1 dm^3) through which carbon monoxide was bubbled for 1 h. The carbon monoxide (Seitetsu Kagaku Co.) used was of 99.9% purity, and all chemicals were of reagent grade.

The platinum electrode modified by Everitt's salt, $K_2Fe^{II}[Fe^{II}(CN)_6]$, was prepared as follows. The Prussian blue $KFe^{III}[Fe^{II}(CN)_6]$ was first electrodeposited on a 6-cm^2 platinum plate from an aqueous solution of 0.01 mol dm^{-3} $FeCl_3$ and 0.01 mol dm^{-3} $K_3[Fe(CN)_6]$, and a film of $K_2Fe^{II}[Fe^{II}(CN)_6]$ was formed by cathodic reduction of the Prussian blue film in the KCl solution. The *i vs. E* curve of the resulting modified platinum electrode exhibited sharp peaks at +0.15 V [*vs.* saturated calomel electrode (s.c.e.)] with a peak separation of

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† *Non-S.I. units employed:* atm = 101 325 Pa, Torr ≈ 133 Pa, cal = 4.184 J.

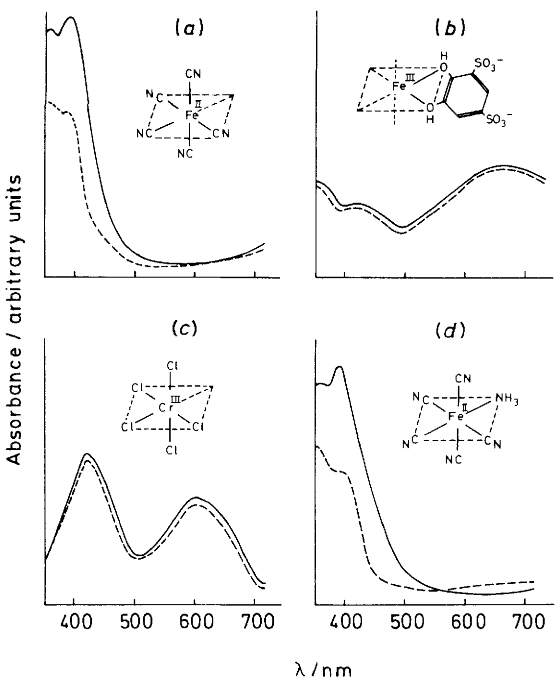


Figure 1. Absorption spectra of catalyst solutions (0.1 mol dm^{-3} KCl, pH 3.5) consisting of 20 mmol dm^{-3} MeOH and (*a*) 5 mmol dm^{-3} $Na_3[Fe(CN)_5]$, (*b*) 1 mmol dm^{-3} Fe^{III} + 2 mmol dm^{-3} 4,5-dihydroxybenzene-1,3-disulphonate, (*c*) 5 mmol dm^{-3} $[NH_4]_2[CrCl_5]$, or (*d*) 5 mmol dm^{-3} $Na_3[Fe(CN)_5(NH_3)]$ with nitrogen or CO (– – – –)

about 10 mV.[21,22] The average amount of the film of $K_2Fe^{II}[Fe^{II}(CN)_6]$ was about 2.8 × 10^{-7} mol cm^{-2} with respect to the concentration of high-spin iron ions.

The electrolytic cell consisted of cathode and anode compartments separated by a fine frit. The cathode compartment was water-jacketed and a constant temperature (±0.5 °C) maintained. The working electrode was the modified platinum electrode, and the counter electrode was a platinum plate with a geometrical area of 10 cm^2. An s.c.e. was connected to the cathodic compartment by means of a Luggin capillary and all potentials are referred to it. The volume of the test solution was 50 cm^3.

All the voltammetric and the electrolysis experiments were done with the usual potentiostat together with a potential programmer. Spectrometric data for the catalysts were obtained with i.r. (Jasco IRA-1), u.v. (Shimazu UV-200), and mass spectrometers (Nippon Densi JMS-D100). The metal complexes were isolated from the catalyst solutions before and after electrolysis, and used to prepare KBr disks for i.r. spectroscopy. The isotope distributions in added and produced methanol were analysed by mass spectrometry. The solutions for this measurement were prepared with D_2O (Merck, 99.75%) instead of water and the pH was adjusted with DCl (Merck, 20% in D_2O).

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 was as follows. The sample solution (2.5 cm^3) was transferred to a cell which was connected to a vacuum through a stopcock. A side-port of the cell was fitted with a rubber septum in order to withdraw samples by a syringe, and the solution was evaporated under 1 Torr pressure at 70 °C. Nitrogen gas was introduced into the cell and gas samples (2 cm^3) were taken with a Pressure-Lock air-tight gas syringe. The calibration curve for this sampling procedure was linear for the quantity of methanol. The amount of methanol produced was calculated from the difference in the methanol content of the initial and the final solutions. A Ohkura model SSC-1 steam chromatograph with steam as the carrier gas, a flame ionization detector, and a Poropak R column was employed. Aqueous samples can be used without any pretreatment.[23] The linearity of the calibration curve obtained by this method was also excellent.

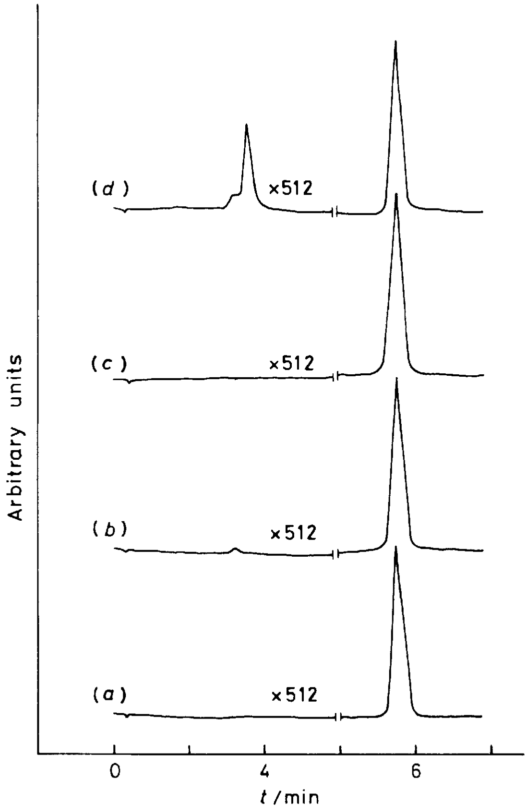


Figure 2. Steam chromatograms of catalyst solutions (0.1 mol dm^{-3} KCl, pH 3.5) consisting of 20 mmol dm^{-3} EtOH and 5 mmol dm^{-3} $K[Cr(C_2O_4)_2]$ with N_2 [(*a*), (*b*)], and CO [(*c*), (*d*)]. Curves: (*a*), (*c*), before electrolysis; (*b*), (*d*), after electrolysis at −0.9 V for 7 h, 40 °C

Formic acid and formaldehyde generated as by-products in the reduction of CO were determined by a colorimetric analysis using chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid) as well by the above two techniques, but their amounts were negligibly small.

Results

Absorption spectra of the catalyst solutions consisting of methanol and various metal complexes are shown in Figure 1. The colours of the solutions were yellow (*a*), dark green (*b*), green (*c*), and yellow (*d*). The solutions with pentacyanoferrate(II) and amminepentacyanoferrate(II) changed from yellow to dark green after CO was introduced, but no change in colour was observed for the solutions containing other metal complexes. The spectral features are similar for solutions with and without CO, but the absorbance tends to decrease in the presence of CO. Although it is difficult to describe the exact structure of the metal complex–MeOH–CO system from these spectra, an interaction between the central metal and CO can be suggested.

The catalytic system consisting of a metal complex and ethanol converted CO into methanol, although the efficiency

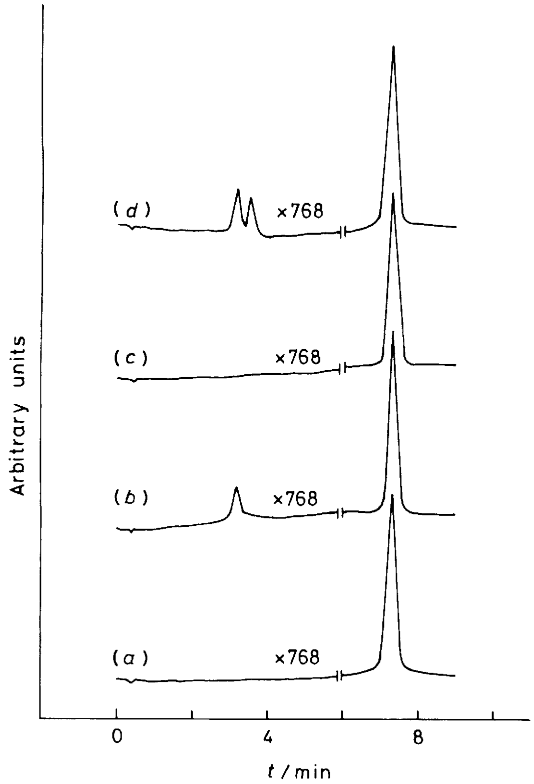


Figure 3. Steam chromatograms of catalyst solutions consisting of 20 mmol dm^{-3} EtOH and 1 mmol dm^{-3} Fe^{III} + 2 mmol dm^{-3} 4,5-dihydroxybenzene-1,3-disulphonate. Details, as in Figure 2, except electrolysis time was 6 h

was much lower than the system involving methanol. Typical steam chromatograms for the catalyst solutions consisting of ethanol and bis(oxalato)chromate(III) or (4,5-dihydroxybenzene-1,3-disulphonato)iron(III) complex are shown in Figures 2 and 3, respectively. Before electrolysis [curves (*a*) and (*c*)] one peak exists at 7.6 min that is assigned to ethanol added initially. After electrolysis [curve (*b*)] in the solutions with N_2 an additional peak appears at 3.3 min. This is ascribed to acetaldehyde produced by electro-oxidation of ethanol in the anodic compartment and diffused into the test cell through the fine frit.[24] In the presence of CO, after electrolysis an additional peak is present at 3.7 min [curve (*d*)] due to methanol. The peak height corresponded to 16.5 and 4.1 μmol dm^{-3}, respectively, in Figures 2 and 3. The current efficiencies estimated from the amounts of methanol produced were 3.68 and 1.63%, respectively. As described below, these values are very small compared to those obtained in the methanol–metal complex system, and can be attributed to the more difficult insertion of CO into the ethanol–metal than into the methanol–metal bond.

The current–time curves observed when a constant potential was applied are shown in Figure 4. The oscillations appear after a certain induction period and are characterized by three parameters: the induction time (τ), amplitude (I_p), and oscillation period (ω). As is seen, no oscillation is observed at 30 °C, and the parameters are dependent markedly on the temperature: τ = 9 (50) and 36.5 min (40 °C); I_p = 10 (50) and 4.2 μA cm^{-2} (40 °C); ω = 8 (50) and 12.5 min (40 °C). As reported previously,[25] however, the oscillation period does not depend on the applied potential, although τ and I_p both do. In most cases, the current oscillation was a function of temperature, applied potential, and the nature and concentration of the metal complex or alcohol added, *etc.* It does not seem to be related to the Belousov–Zabotinskii system[26] since our oscillation requires heterogeneous as well as homogeneous phases. The oscillation observed is probably caused by the disappearance and the recovery of the film of Everitt's salt.[25]

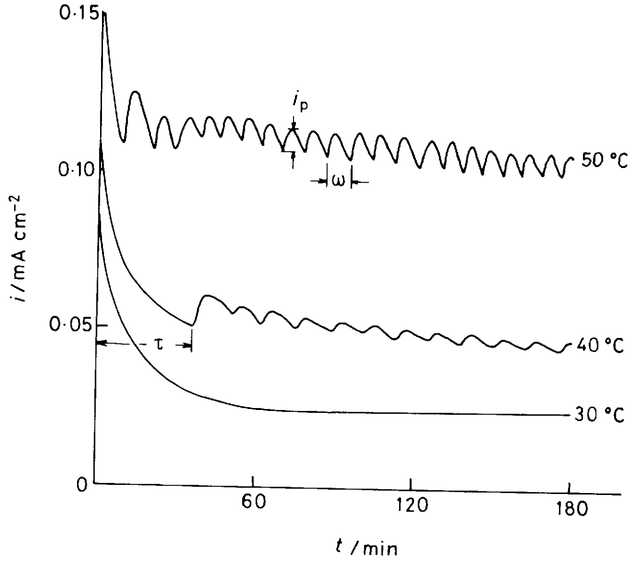


Figure 4. Current *vs.* time curves at −0.9 V for a 0.1 mol dm^{-3} KCl solution in the presence of CO. Initial conditions: 5 mmol dm^{-3} K[Cr(C_2O_4)$_2$], 20 mmol dm^{-3} MeOH, pH 3.5

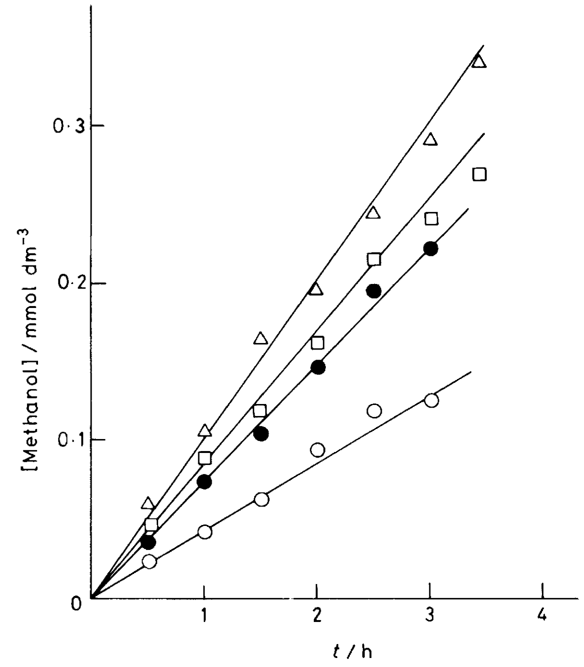


Figure 5. Methanol formation as a function of time in the catalyst systems of 20 mmol dm^{-3} methanol with 1 mmol dm^{-3} (4,5-dihydroxybenzene-1,3-disulphonato)iron(III) (△), 5 mmol dm^{-3} pentachlorochromate(III) (□), 5 mmol dm^{-3} pentafluoroferrate(III) (●), or 5 mmol dm^{-3} amminepentacyanoferrate(II) (○). Electrolysis potential, −0.9 V; pH 3.5; 30 °C

As shown in Figure 5, the concentration of methanol produced increases linearly with the cathodizing time. The initial rate of reaction was estimated from the slope to be dependent on the nature of the added metal complex. A linear

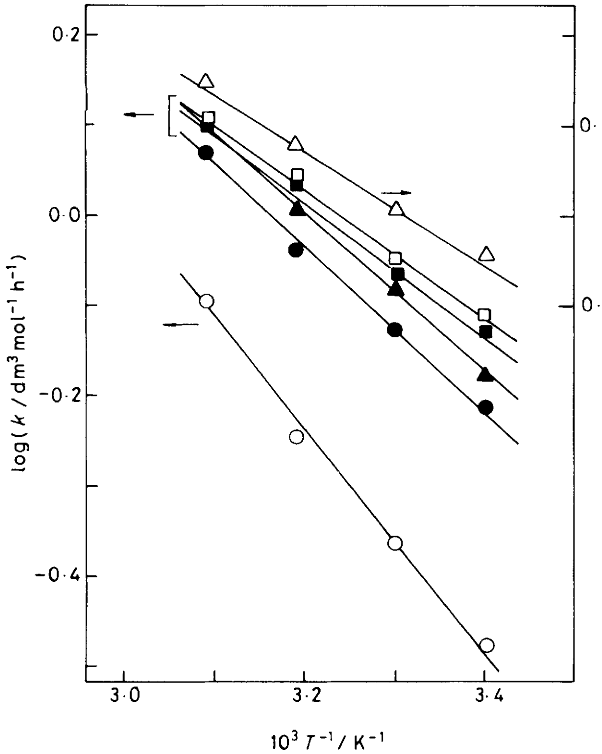


Figure 6. Arrhenius plot of methanol formation. Catalyst systems as in Figure 5 except for 5 mmol dm^{-3} bis(oxalato)chromate(III) (■) and 5 mmol dm^{-3} pentacyanoferrate(II) (▲). Electrolysis potential, −0.9 V; pH 3.5

relationship also held between the concentrations of methanol produced and those of the metal complex or alcohol added,[16] and the initial rate of methanol formation is given by equation (1) where k is the pseudo-rate constant and [ML] and [ROH]

$$v = k[\mathrm{ML}][\mathrm{ROH}] \qquad (1)$$

are the concentrations of the metal complex and primary alcohol added, respectively.

The Arrhenius plot of the pseudo-rate constants is shown in Figure 6. The corresponding activation energies are given in the Table together with the amount of methanol produced, the amount (Q) of electric charge passed, the current efficiency (η_i), and the pseudo-rate constant. The activation energy is influenced by the nature of metal complex: its value is smallest in the presence of the (4,5-dihydroxybenzene-1,3-disulphonato)-iron(III) complex, and increases in the order pentachlorochromate(III), bis(oxalato)chromate(III), pentacyanoferrate(II), pentafluoroferrate(III), and amminepentacyanoferrate(II). As shown in the Table, the current efficiency in the solutions containing pentachlorochromate(III) and pentafluoroferrate(II) is much lower than those with the other four metal complexes. This is due to more vigorous hydrogen evolution in the first two solutions. The extent of methanol formation is lowest in the presence of amminepentacyanoferrate(II). Similar experiments were performed with hexacyanoferrate(II) and pentacyanonitrosylferrate(II), however no methanol was detected. Hence the general feature of a metal complex capable of operating as a catalyst in the CO reduction is that it should have at least one vacancy (associated with a water molecule in aqueous solution) in its co-ordination shell which can be occupied by a new ligand during the course of reaction.

Infrared spectra of the (4,5-dihydroxybenzene-1,3-disulphonato)iron(III) complex isolated from the catalyst solutions are shown in Figure 7. Curves (a) and (b) are for samples isolated from the solutions in the presence of N_2 and CO, respectively; (c) is for the species isolated from the solution with CO after electrolysis at −0.9 V for 3 h. There is no conspicuous difference between curves (a) and (b); however, in curve (c) two weak bands appear at 1 090 and 1 180 cm^{-1} which could be attributed to the stretching vibration of C–O–C in methyl formate. These bands have been also observed for a sample isolated from the catalyst solution containing pentacyanoferrate(II).[27] It is therefore suggested that the reduction of CO to methanol proceeds *via* methyl formate as an intermediate, and moreover that the metal complex does not undergo degradation during the course of electrolysis.

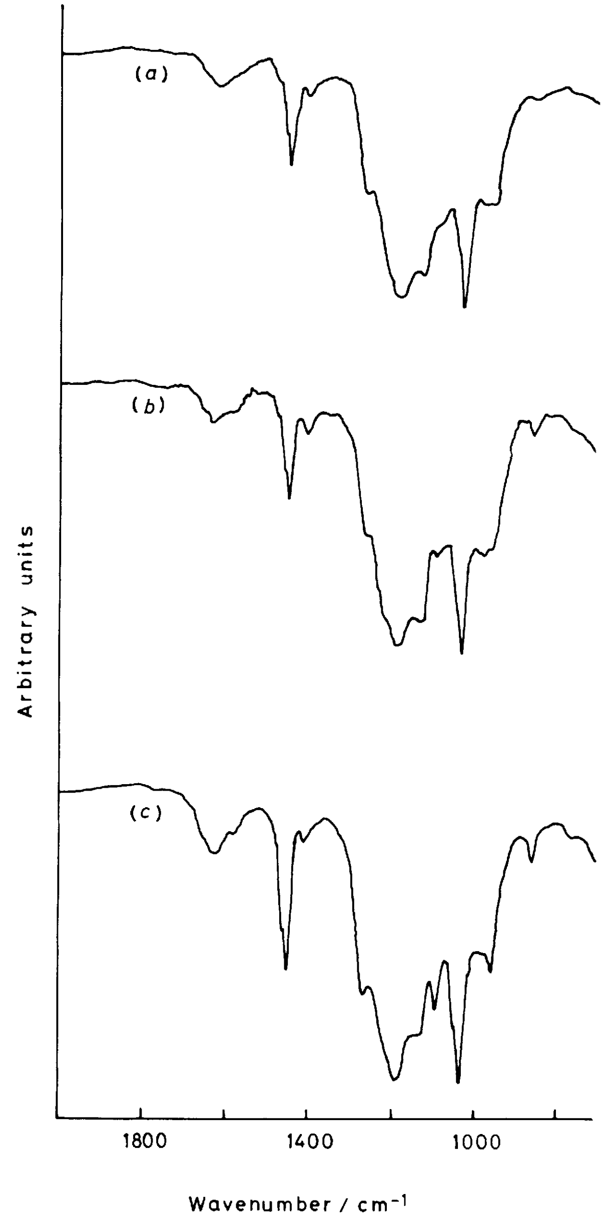


Figure 7. I.r. spectra of the metal complexes isolated from the catalyst solutions (pH 3.5; 1 mmol dm^{-3} Fe^{3+}, 2 mmol dm^{-3} 4,5-dihydroxybenzene-1,3-disulphonate, 20 mmol dm^{-3}, methanol in the presence of N_2 [(a)] and CO [(b), (c)]. (a), (b), Before electrolysis; (c), after electrolysis at 40 °C and −0.9 V for 3 h

Table. The amount of methanol produced, the amount (Q) of electric charge passed, the current efficiency (η_i), the pseudo-rate constant (k), and the activation energy (E_a)[a]

Complex[b]	Methanol concentration[c]/ mmol dm^{-3}	Q^c/C	η_i^c/%	k^c/ dm^3 mol^{-1} h^{-1}	E_a/ kcal mol^{-1}
d	0.278	4.632	115.8	5.90	2.91
$[NH_4]_2[CrCl_5]$	0.249	8.857	52.3	1.10	3.25
$K[Cr(C_2O_4)_2]$	0.202	3.721	104.8	1.09	3.44
$Na_3[Fe(CN)_5]$	0.20	3.575	108.0	1.00	4.06
$K_2[FeF_5]$	0.198	11.582	33.0	0.91	4.21
$Na_3[Fe(CN)_5(NH_3)]$	0.115	2.732	81.3	0.56	5.83

[a] The volume of the test solution, 50 cm^3; added CH_3OH, 20 mmol dm^{-3}; pH, 3.5; electrolysis potential, −0.9 V; time, 3 h. [b] Concentration 5 mmol dm^{-3}, unless stated otherwise. [c] Temperature, 40 °C. [d] 1 mmol dm^{-3} Iron(III) + 2 mmol dm^{-3} 4,5-dihydroxybenzene-1,3-disulphonate.

Discussion

The reduction of CO to methanol in the presence of methanol and a metal complex was confirmed by the mass spectrometric method. In this experiment, the catalyst solution contained a metal complex, MeOH, KCl, D_2O, and DCl. For the initial solution of 0.1 mol dm^{-3} KCl–D_2O with MeOH, two peaks were seen at *m/e* 31 and 32 corresponding to MeO and MeOH. After electrolysis for 3 h, however, three additional peaks were present at *m/e* 33, 34, and 36 which are ascribed to MeOD, CD_3O, and CD_3OD, respectively. This result definitely proves that CO is convertible into methanol by the present process. Supporting evidence was provided by the appearance of the methanol peak in the steam chromatograms (Figures 2 and 3) where the catalyst solutions comprised ethanol and a metal complex.

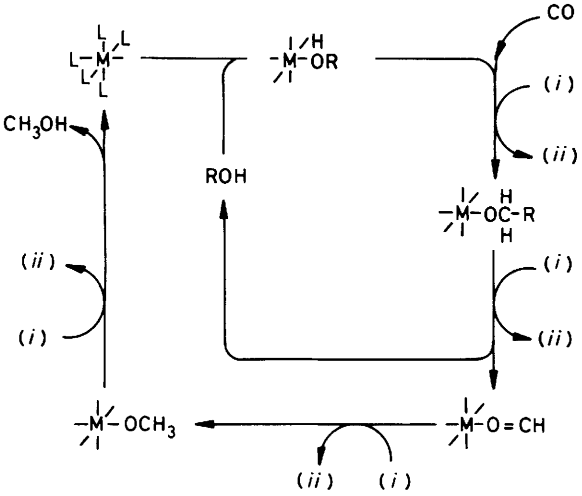
In catalyst solutions containing either a metal complex or a primary alcohol, CO could not be reduced to methanol. Even in the presence of both a metal complex and an alcohol the reduction did not take place at a bright platinum electrode. Hence the use of Everitt's salt as a mediator, and of a metal complex and a primary alcohol as homogeneous catalysts for the conversion of CO into methanol. The overall reaction has been proposed[15] to be as in equation (2). The reduction of CO is caused by the oxidation of high-spin iron(II) ions to high-spin iron(III) ions. The methanol formation naturally terminates when the oxidation reaches equilibrium. If the Prussian blue is reduced by means of the electrochemical technique back to Everitt's salt, however, the coated film again becomes able to operate as a mediator and the conversion continues.

$$CO + 4H^+ + 4K_2Fe^{II}[Fe^{II}(CN)_6] \rightleftharpoons MeOH + 4KFe^{III}[Fe^{II}(CN)_6] + 4K^+ \quad (2)$$

As described above, a metal complex capable of operating as a catalyst in the CO reduction must have at least one vacancy in its co-ordination shell which can be occupied by a new ligand. I.r. spectra indicate that the reduction of CO takes place *via* methyl formate as an intermediate.

The occurrence of the current oscillation can be explained as follows. Reaction (2) of CO with Everitt's salt may lead to a decrease in the amount of the latter, and an increase in the amount of Prussian blue. To maintain a constant potential the reduction current for the Prussian blue must be increased; whereupon the Everitt's salt is formed, and the reduction current falls to the initial level. The rates of disappearance and recovery of Everitt's salt, affecting τ, I_p, and ω, may be limited by mass transfer in solution.[25]

These experimental results are consistent with the reaction mechanism shown in the Scheme. The net reaction is as in equation (2), and the formation of methyl formate is assumed.



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

As shown in the Table, the current efficiency for methanol formation was lower in the presence of pentachlorochromate(III) and pentafluoroferrate(III). This may be caused by the slight decomposition of these complexes during the electrolysis, as confirmed by deposition of the metals on the film of Everitt's salt after electrolysis, *i.e.* a decrease in the amount of active metal complex leads to a suppression of the catalytic process and hydrogen evolution becomes predominant in the cathodic reactions. The activation energy for the formation of methanol was 2.9—5.8 kcal mol^{-1}, and the reaction rate is limited by mass transfer in solution. The rate-determining step is presumably the diffusion of the intermediate species towards the film of Everitt's salt where an electron is transferred.

Further studies will be directed to clarifying the homogeneous catalysis and examining different electrode mediators.

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