Electrocatalytic Reduction of Carbon Dioxide to Methanol. Part 2.[1] Effects of Metal Complex and Primary Alcohol*

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The conversion of CO_2 into methanol by Everitt's salt, $K_2Fe^{II}[Fe^{II}(CN)_6]$, has been studied in the presence of various metal complexes and primary alcohols. The activation energies for the methanol formation were 5.8—10.6 kcal mol^{-1}, approximately twice those for the reduction of CO. The i.r. spectra of the metal complexes indicated that the reduction of CO_2 takes place *via* a formate-type intermediate. The mechanism is considered to be very similar to that for reduction of CO, but the reduction of CO_2 appears to be more dominated by its insertion into a M(central metal)–OR(primary alcohol) bond than is that of CO.

The conversion of carbon dioxide into organic products is an important goal in the development of alternative fuel sources. There have been many attempts to find non-biological approaches to the reduction of carbon dioxide. The conversion methods presented so far involve hydrogenation utilizing homogeneous and heterogeneous catalysis, electrochemical reduction on metal electrodes, and photochemical or photoelectrochemical reduction. Although the reduction of carbon monoxide by molecular hydrogen has been extensively studied, little attention has been paid to that of carbon dioxide. A few studies on hydrogenation in homogeneous or heterogeneous catalysis have concerned the formation of alkyl formates from carbon dioxide using anionic carbonyl hydrides[2] and the conversion of carbon dioxide into methanol over supported palladium[3] or rhenium[4] catalysts. These reactions require severe conditions, *i.e.* high temperature (> 100 °C) and pressure (> 10 atm).

The electrochemical conversion has been assumed to be the best possible method, and many attempts have been made by using metal electrodes. The major reduction product in aqueous solution is formic acid, but further reduction is very difficult. The metal electrodes with high hydrogen overpotential and low point of zero charge are efficient as the electrocatalyst. The electrode materials used include mercury or amalgamated metal,[5-7] lead,[8-10] zinc,[11,12] tin,[12,13] indium,[12,13] ruthenium,[14] platinized titanium dioxide,[15] or n-type gallium arsenide.[16] A shortcoming of this method is that it requires large overpotentials, making it an inefficient consumer of energy. Hence, to overcome this shortcoming, several investigators have tried the electrochemical reduction of carbon dioxide with the assistance of homogeneous catalysis,[17-22] a mediator on an electrode,[23] or irradiation by light.[24-32] Many problems still await solution, *e.g.* low yield of products, lack of selectivity for the desired compound, worthless products, or high production costs.

We have found [1] a catalytic conversion process in which CO_2 is reduced to methanol by Everitt's salt at ordinary temperatures in the presence of a metal complex and primary alcohol. This process is an indirect electrochemical one, and was originally discovered for the CO conversion.[33-36] Following the preliminary experiment[1] on CO_2 reduction, we have undertaken a systematic study under different conditions and now describe the results obtained.

Experimental

The catalyst solutions were prepared by dissolving a metal complex and primary alcohol in 0.1 mol dm^{-3} KCl. The metal complexes used were diaquabis(oxalato)chromate(III), $K[Cr(C_2O_4)_2(H_2O)_2]$,[37] aquapentacyanoferrate(II), $Na_3[Fe(CN)_5(H_2O)]$,[38] aquapentachlorochromate(III), $[NH_4]_2[CrCl_5(H_2O)]$,[39] and bis-(4,5-dihydroxybenzene-1,3-disulphonato)ferrate(III), $[Fe\{C_6H_2(OH)_2(SO_3)_2\}_2]^-$. The last was prepared by dissolving a given amount of purified ammonium iron(III) sulphate and the benzene disulphonate in 0.1 mol dm^{-3} KCl. The primary alcohols used were methanol and ethanol. The catalyst solutions were kept in a storage vessel of 1 dm^3 saturated with CO_2 by bubbling for 1 h. The carbon dioxide (Iwatani Co.) used was of 99.7% purity, and all chemicals were of reagent grade.

Everitt's salt, $K_2Fe^{II}[Fe^{II}(CN)_6]$, coated on a platinum plate (6 cm^2) was prepared by electroreduction of a film of Prussian blue, $KFe^{III}[Fe^{II}(CN)_6]$, deposited on the substrate from an aqueous $Fe[Fe(CN)_6]$ solution.[40,41] The average amount of the film of Everitt's salt was about 2.7×10^{-7} mol cm^{-2}.

The electrolytic cell had two compartments separated by a fine-porosity glass frit. The main compartment was water-jacketed and a constant temperature (± 0.5 °C) was maintained. This compartment contained the above modified platinum electrode, and the other one a platinum-plate counter electrode. All electrochemical experiments were done with the usual potentiostat and a potential programmer. Spectrometric data for the catalysts were obtained with i.r. (Jasco IRA-1) and u.v. spectrometers (Shimazu UV-200). The metal complexes were isolated from the catalyst solutions before and after electrolysis, and KBr disc pellets were prepared for i.r. spectroscopy.

Methanol was determined by both gas and steam chromatographic methods. A JGC-100 gas chromatograph equipped with a thermal conductivity detector and a Poropak Q column was employed. The sampling procedure was described previously.[33] The steam chromatograph was an Ohkura model SSC-1 which employs steam as the carrier gas with a flame ionization detector and a Poropak R column,[42] and the aqueous sample was used without any pretreatment.

Results and Discussion

Steam chromatograms of the catalyst solutions containing the $[Fe\{C_6H_2(OH)_2(SO_3)_2\}_2]^-$ complex and ethanol are shown in Figure 1. Curve (*a*) was obtained before electrolysis, and (*b*) and (*c*) are after electrolysis for 3 and 6 h, respectively. In all curves, the peak at 7.6 min is attributed to ethanol added initially. In curves (*b*) and (*c*), two additional peaks appear at 3.3 and 3.7 min. The first is ascribed to acetaldehyde produced by electro-oxidation of ethanol in the anodic compartment which leaks to the test cell through the fine frit.[1] The second peak is due to methanol, and the peak height after electrolysis for 6 h is

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* *Non-S.I. units employed*: atm = 101 325 Pa; cal = 4.184 J.

equivalent to 2.3 µmol dm^{-3}. This result confirms that CO_2 can be reduced to methanol by the proposed conversion process. The reduction of CO_2 can be represented by a similar reaction to that of CO[33] [equation (1)]. As for the reduction of CO,[33] however, reaction (1) can be activated only by the presence of a metal complex and primary alcohol. In order to reduce CO_2 continuously, Prussian blue is required to be rereduced to Everitt's salt by an external source of energy. Reaction (1) can take place if the electrode potential is polarized so that the Prussian blue film is reducible to Everitt's salt [< +0.15 V *vs.* saturated calomel electrode (s.c.e.)]. In general, the direct electrochemical reduction of CO_2 at a metal electrode needs large overpotentials (about −2.0 V *vs.* s.c.e.), and hence reaction (1) results in a considerable lowering of the overpotential for the reduction of CO_2.

$$CO_2 + 6K_2Fe^{II}[Fe^{II}(CN)_6] + 6H^+ \rightleftharpoons CH_3OH + 6KFe^{III}[Fe^{II}(CN)_6] + 6K^+ + H_2O \quad (1)$$

The yield of methanol in the CO_2 conversion was very low for the catalyst solution containing ethanol, although the evidence for the conversion is more direct. The use of methanol in place of ethanol resulted in a much improved conversion of CO_2 into methanol. As shown in Figure 2, the methanol formation is linearly related to the reaction time. At longer electrolysis times and higher temperatures, the lines become curved, presumably due to exhaustion of the reactant CO_2 or to leakage of the methanol produced from the reaction compartment.

The turnover frequency of CO_2 conversion into methanol, N_m, defined as the number of moles of methanol produced per mol of metal complex per hour, is plotted against reciprocal temperature in Figure 3, and the corresponding activation

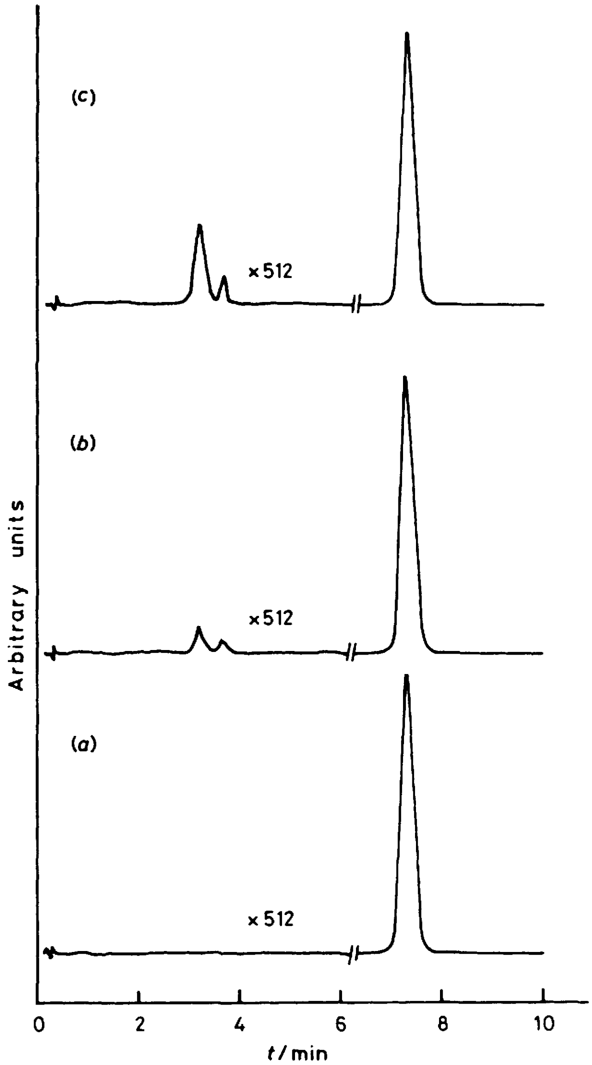


Figure 1. Steam chromatograms of the catalyst solutions (0.1 mol dm^{-3} KCl, pH 3.5, 40 °C) containing 4 mmol dm^{-3} Fe^{III}–8 mmol dm^{-3} $C_6H_2(OH)_2(SO_3)_2^{2-}$ and 20 mmol dm^{-3} ethanol before (*a*) and after electrolysis for 3 (*b*) and 6 h (*c*) at −1.0 V *vs.* s.c.e.

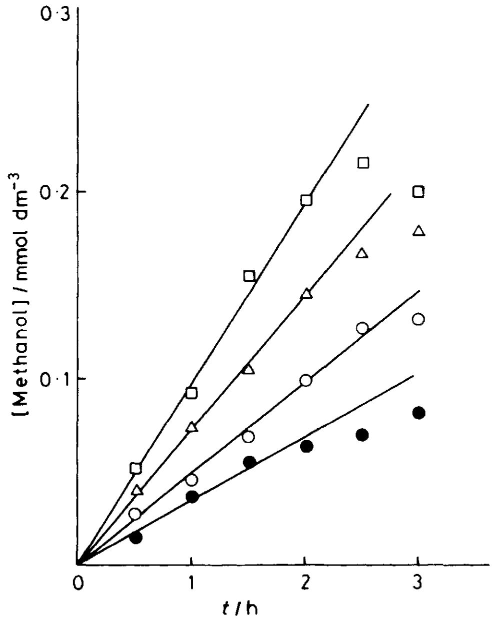


Figure 2. Methanol formation as a function of time in a solution with 20 mmol dm^{-3} methanol and 5 mmol dm^{-3} pentacyanoferrate(II). Electrolysis potential, −0.9 V *vs.* s.c.e.; pH 3.5. Temperature: 20 (●), 30 (○), 40 (△), and 50 °C (□)

Table. Electric charge (Q) passed, concentration of methanol produced, current efficiency (η_i), turnover frequency (N_m), and activation energy (E_a)

Complex	Concentration (mmol dm^{-3})	Primary alcohol	Potential (V *vs.* s.c.e.)	Q^a/C	Methanol[a] produced (µmol dm^{-3})	$\eta_i{}^a$/ %	$10^3N_m{}^b$/ h^{-1}	E_a/ kcal mol^{-1}
$[Fe\{C_6H_2(OH)_2(SO_3)_2\}_2]^-$	1	CH_3OH	−0.9	32.2	161	14.5	89	5.8
$Na_3[Fe(CN)_5(H_2O)]$	5	CH_3OH	−0.9	27.5	148	15.5	15	7.0
$K[Cr(C_2O_4)_2(H_2O)_2]$	5	CH_3OH	−0.9	31.8	159	14.5	16	5.8
$[Fe\{C_6H_2(OH)_2(SO_3)_2\}_2]^-$	4	C_2H_5OH	−1.0	51.4	1.1	0.06	0.094	8.9
$[NH_4]_2[CrCl_5(H_2O)]$	10	C_2H_5OH	−1.0	90.7	1.4	0.05	0.045	7.9
$K[Cr(C_2O_4)_2(H_2O)_2]$	10	C_2H_5OH	−1.0	64.8	0.9	0.04	0.030	10.6

[a] At 40 °C; electrolysis time, 3 h. [b] At 40 °C.

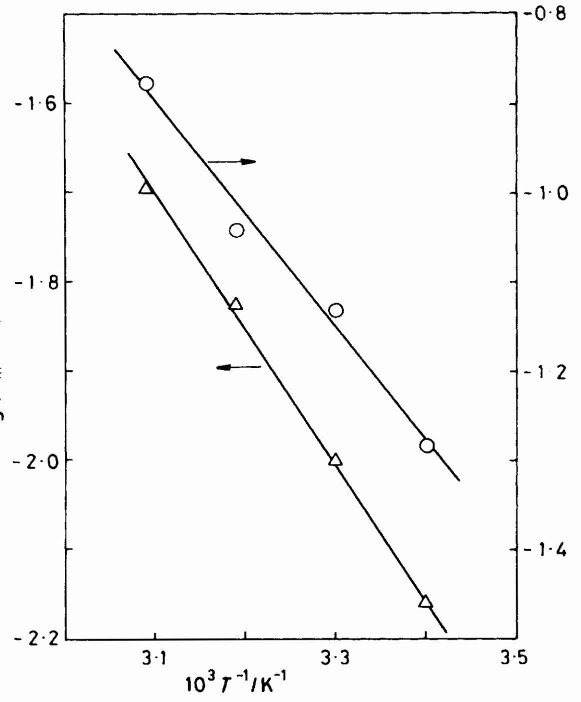
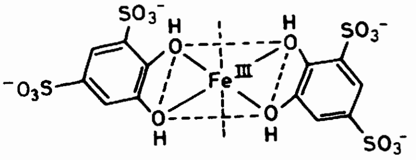


Figure 3. Arrhenius plot of the turnover frequency, N_m, for methanol formation in a solution with 20 mmol dm^{-3} methanol and 5 mmol dm^{-3} pentacyanoferrate(II) (△) or 1 mmol dm^{-3} Fe^{III}–2 mmol dm^{-3} $C_6H_2(OH)_2(SO_3)_2{}^{2-}$ (○)

energies were 5.8 and 7.0 kcal mol^{-1} for catalyst solutions containing $[Fe\{C_6H_2(OH)_2(SO_3)_2\}_2]^-$ and pentacyanoferrate(II), respectively. The activation energies under various conditions, along with the electric charge (Q) passed, concentration of methanol produced, current efficiency (η_i), and turnover frequency are given in the Table. These values are considerably dependent on the nature of the metal complex and alcohol used. As pointed out previously,[36] a metal complex capable of operating as the homogeneous catalyst in the present reaction system should have at least one vacancy (associated with a water molecule in aqueous solution) in its co-ordination shell. For example, the complex $[Fe\{C_6H_2(OH)_2(SO_3)_2\}_2]^-$ has structure (I) in which the ligand is bidentate, forming the 1:2 complex with Fe^{III} at a pH value of about 4.[43] In this structure there are two vacancies on the z axis. In more acidic or alkaline solutions, however, the ligand forms a 1:1 or 1:3 complex with Fe^{III}. Whenever a complex of this ligand with Fe^{III} acts as a catalyst there is at least one vacancy in the co-ordination shell.



(I)

The catalyst solutions containing CH_3OH give larger values of η_i and lower values of E_a. In the case of CO,[36] *e.g.* at 1 mmol dm^{-3} Fe^{III}, 2 mmol dm^{-3} $C_6H_2(OH)_2(SO_3)_2{}^{2-}$, and 20 mmol dm^{-3} CH_3OH, the concentration of methanol produced was 0.278 mmol dm^{-3}, Q = 4.632 C, η_i = 115.8%, $N_m = 92 \times 10^{-3}$ h^{-1}, and E_a = 2.9 kcal mol^{-1}. From the values in the Table, it is seen that the conversion of CO_2 is more difficult. The cause of this is discussed later. In the solutions with C_2H_5OH, the amount of methanol formed, η_i, and N_m are much smaller; however, it is obvious that CO_2 is also convertible into methanol in the presence of different metal complexes. As shown in the Table, the activation energies are 5.8—10.6 kcal mol^{-1} which are approximately twice those for the conversion of CO.[36] In the latter case the reaction rate was considered to be limited by mass transfer. The activation energies obtained here seem to be higher than those for mass-transfer control in solution. Hence it may be reasonable to assume that the reduction of CO_2 is controlled by a chemical reaction step.

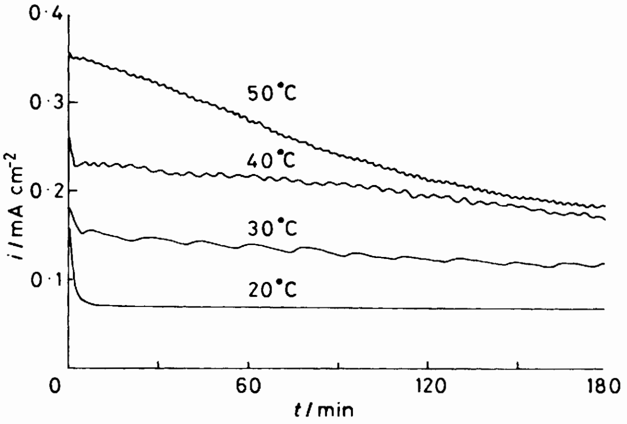


Figure 4. Current oscillations at various temperatures in a 0.1 mol dm^{-3} KCl solution containing 1 mmol dm^{-3} Fe^{III}–2 mmol dm^{-3} $C_6H_2(OH)_2(SO_3)_2{}^{2-}$ and 20 mmol dm^{-3} methanol. Electrode potential, −0.9 V *vs.* s.c.e.; pH 3.5

Current–time curves measured during the electrolysis at a constant potential are shown in Figure 4. The current oscillations observed can be characterized by three parameters: induction time (τ), amplitude (I_p), and oscillation period (ω). It is seen from this figure that no oscillation is present at 20 °C, and τ and ω depend considerably on the temperature of the solution: τ = 1 (50), 2.5 (40), and 5 min (30 °C); ω = 2.5 (50), 5 (40), and 17.5 min (30 °C). However, I_p is not very sensitive to the temperature: 3.1 (50), 3.3 (40), and 3.3 μA cm^{-2} (30 °C). Similar results were obtained in the reduction of CO[44] although the values of τ, ω, and I_p are very different, *e.g.* at 50 °C, τ = 9 min, I_p = 10 μA cm^{-2}, and ω = 8 min. As reaction (1) proceeds, the concentrations of both Everitt's salt and the electrolysed substance decrease on the electrode surface, and the external current diminishes. The reaction products diffuse away from the surface, and the concentration of Everitt's salt is restored to its former level by reduction of Prussian blue, which leads to an increase in current. The current oscillation observed may be related to these processes. The magnitude of I_p obtained here was much smaller than that in the case of CO, which again suggests that a chemical reaction is more significant than mass transfer in the reduction of CO_2.

I.r. spectra of the Fe^{III}–$C_6H_2(OH)_2(SO_3)_2{}^{2-}$ complexes isolated from the catalyst solutions before [curves (*a*), (*b*)] and after [curve (*c*)] electrolysis are shown in Figure 5. Curves (*a*) and (*b*), (*c*) are for the metal complexes isolated from solutions saturated with N_2 and CO_2, respectively. Curves (*a*) and (*b*) are similar. In curve (*c*), however, two bands appear at 1 090 and 1 180 cm^{-1} (arrowed) which are attributable to the C–O–C stretching vibration like that in a formate. These two bands have been also observed in the conversion of CO.[36] It is therefore suggested that the conversion of CO_2 into methanol takes place *via* a formate-type intermediate, and the metal

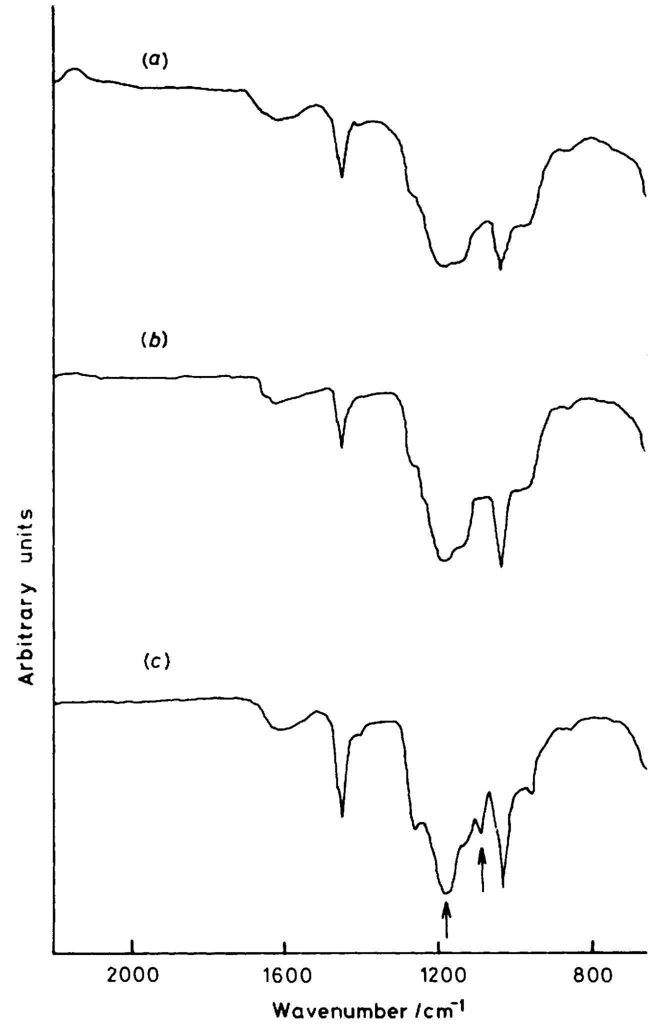
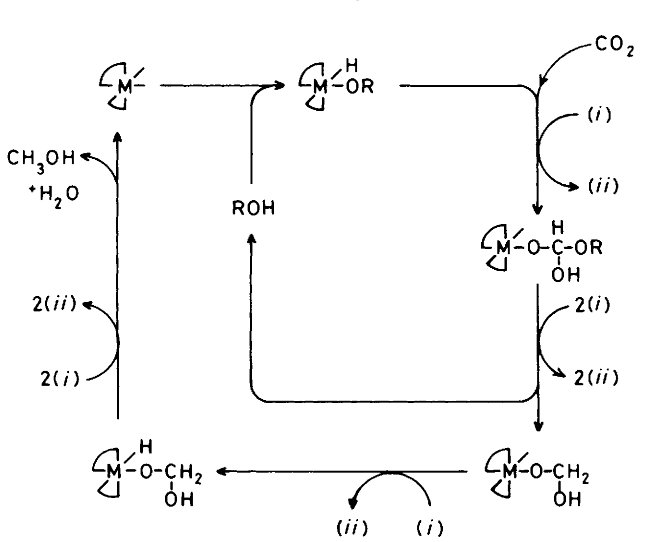


Figure 5. I.r. spectra of the metal complexes isolated from a catalyst solution [pH 3.5, 1 mmol dm^{-3} Fe^{III}, 2 mmol dm^{-3} $C_6H_2(OH)_2(SO_3)_2^{2-}$, 20 mmol dm^{-3} ethanol] saturated with N_2 (*a*) and CO_2 (*b*), (*c*). (*a*), (*b*) Before electrolysis; (*c*) after electrolysis for 3 h at a potential of −1.0 V *vs.* s.c.e. and 40 °C

complex operating as the catalyst suffers no degradation during the electrolysis. A detailed mechanism for reaction (1) is shown in the Scheme.

This scheme is very similar to that proposed for the CO reduction.[33] A co-ordination bond is first formed between a central metal and a primary alcohol, CO_2 inserts into this bond to form a formate-type intermediate, and eventually methanol and the initial complex are produced by the reaction with Everitt's salt. Compared with the reduction of CO, the yield and current efficiency for methanol formation are low, and this trend is more marked when ethanol is used as the primary alcohol. The major cause may be the difficulty of inserting CO_2 into the M–OR bond. This reaction seems not to be difficult in the case of CO as the value of the activation energy obtained suggests mass-transfer control.[36] The difficulty of the CO_2 insertion, especially in the presence of ethanol, may be due to steric hindrance. In fact, the formation of methanol was much reduced in the presence of secondary and tertiary alcohols. Therefore, the CO_2 insertion reaction should be more activated in order to obtain a higher yield and current efficiency of methanol formation.



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

It is concluded that CO_2 can be reduced to methanol by Everitt's salt in the presence of a primary alcohol and metal complex, and the mechanism is essentially identical to that of CO reduction. However, the reaction of CO_2 is more dominated by its insertion into a M–OR bond than is that of CO.

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