Selective Formation of $HCOO^-$ in the Electrochemical CO_2 Reduction catalysed by $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridine)

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The selectivity for the formation of $HCOO^-$ in electrochemical CO_2 reduction catalysed by $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridine) increases on increasing the pK_a value of the proton source, and highly selective formation of $HCOO^-$ is achieved by using $Me_2NH{\cdot}HCl$ or PhOH as a proton source in MeCN.

Electrochemical CO_2 reductions catalysed by transition metal complexes have been reported,[1,2] and the reduction products are mostly mixtures of $HCOO^-$ and CO resulting from the reactions of equations (1) and (2), or only CO. However, selective formation of $HCOO^-$ has scarcely been reported.[2] Thus, selective $HCOO^-$ formation with a large current density is required in electrochemical CO_2 reduction since the rate of electrochemical reactions is generally slow. We have recently reported that CO_2 reduction catalysed by $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridine) produced a mixture of CO and $HCOO^-$ (*ca.* 7 : 10) under controlled potential electrolysis at −1.50 V *vs.* standard calomel electrode (s.c.e.) in a dimethylformamide (DMF)–H_2O (1 : 9 v/v) solution buffered at pH 9.5, while only CO was formed at pH 6.0 under otherwise identical electrolysis conditions.[1a,b] In strong alkaline media, however, the reduction of CO_2 is unfavourable owing to the conversion of CO_2 into HCO_3^- and CO_3^{2-}, both of which are inactive towards electrochemical reduction catalysed by $[Ru(bpy)_2(CO)_2]^{2+}$. We now describe the electrochemical CO_2 reduction catalysed by $[Ru(bpy)_2(CO)_2]^{2+}$ in MeOH or MeCN in the presence of several proton sources, where very selective formation of $HCOO^-$ with a fast reaction rate is accomplished.

The electrolysis cell used in this study is essentially the same as described elsewhere[1b,3] except that the anode and cathode compartments were separated by a Nafion membrane in place of a glass filter. A Hg pool (3.1 cm^2) and a platinum plate (*ca.* 3 cm^2) were used as working and auxiliary electrodes,

Table 1. The electrochemical CO_2 reduction catalysed by $[Ru(bpy)_2(CO)_2]^{2+}$ in the presence of several proton sources in MeCN.[a]

Proton source[b]	pK_a[c] in MeCN	Product[d]/μmol $HCOO^-$	CO	H_2	Current density[e] /mA cm^{-2}
$MeNH_2{\cdot}HCl$	15.6	332 (64.1)	103 (19.9)	17 (3.3)	1.6
$Me_2NH{\cdot}HCl$	15.8	437 (84.3)	13 (2.4)	35 (6.8)	3.3
$Me_3N{\cdot}HCl$	14.8	288 (55.5)	32 (6.1)	158 (30.5)	3.3
$PhCO_2H$	12.0	117 (22.5)	51 (9.9)	263 (50.7)	2.2
PhOH	[f]	420 (81.0)	84 (16.3)	2 (0.3)	2.3

[a] Electrode potential was −1.30 V *vs.* s.c.e. [b] 0.20 mol dm^{-3}. [c] G. Charlot and B. Tretmillon, 'Chemical Reactions in Solvents and Melts,' Pergamon Press, New York, 1969. [d] The current efficiency (%) for the formation of the product after the consumption of 100 C in parenthesis. [e] Average value for 100 C. [f] No available data in the literature.

respectively. The reduction of CO_2 in CO_2-saturated MeOH or MeCN (20 cm^3) containing $[Ru(bpy)_2(CO)_2]^{2+}$ (5.0×10^{-4} mol dm^{-3}) and $Bu^n{}_4NClO_4$ (0.10 mol dm^{-3}) as an electrolyte was carried out by controlled potential electrolyses at −1.30 V or −1.50 V *vs.* s.c.e. on an Hg electrode. The reduction products, CO and H_2, were analysed by a gas chromatograph and $HCOO^-$ was determined by an isotachophoretic analyser.[4]

$$CO_2 + H^+ + 2e \rightarrow HCOO^- \qquad (1)$$

$$CO_2 + 2H^+ + 2e \rightarrow CO + H_2O \qquad (2)$$

The reactions of equations (1) and (2) catalysed by $[Ru(bpy)_2(CO)_2]^{2+}$ proceeded smoothly in CO_2-saturated MeOH under controlled potential electrolysis at −1.50 V *vs.* s.c.e. The current efficiency (η) for the formation of $HCOO^-$ and CO after consumption of 100 C were 52.5 and 32.0%, respectively, of which the former value is larger than that in water at pH 9.5 [$\eta(HCOO^-) = 34.0\%$].[1a,b] The $\eta(HCOO^-)$ value increased to 67.7% on reduction of CO_2 in MeOH containing MeONa (0.1 mol dm^{-3}) under the same electrolysis conditions, suggesting that less protic conditions improve the selectivity for the formation of $HCOO^-$, being similar to those for the reduction in aqueous solutions.

The effect of several proton sources with different pK_a values on the reduction of CO_2, therefore, was examined in anhydrous MeCN. The results on the electrochemical CO_2 reduction at −1.30 V *vs.* s.c.e. in MeCN are summarised in Table 1, and show that the relative amounts of reduction products, $HCOO^-$, CO, and H_2 are largely dependent on the pK_a value of proton sources; the $\eta(HCOO^-)$ value increases on increasing the pK_a value, and reaches 84.3% in the presence of $Me_2NH{\cdot}HCl$. Such high selectivity for $HCOO^-$ formation is comparable with that for the reduction of HCO_3^- by a viologen polymer-coated Pd electrode (*ca.* 85%) which is the largest $\eta(HCOO^-)$ value reported so far.[2] In addition, the present reaction is very fast, as inferred from the large current densities of 1.6—3.3 mA cm^{-2} (Table 1), which are in contrast with those for the reduction of HCO_3^- (50—100 $\mu A\ cm^{-2}$).[2] Thus, the present electrochemical CO_2 reduction is one of the most selective for $HCOO^-$ formation, with the fastest reaction rate reported so far.

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