

Session : 1

EPREUVE :
Electrochimie Moléculaire

Durée : 01h00

I – a) Listez les avantages et les inconvénients de l'utilisation de l'électrochimie en synthèse organique.

b) En quoi consiste le procédé d'électrosynthèse MONSANTO ? En rappeler les principes réactionnels (réactions aux électrodes, réactions parasites, nature et influence de l'électrolyte support), ainsi que les éléments les plus essentiels du montage d'électrolyse.

II – *L'article reproduit ci-après a pour objet de nouveaux catalyseurs moléculaires pour la réduction électrochimique du dioxyde de carbone.*

a) Citer d'autres exemples de réactions inorganiques qui peuvent être catalysées selon une voie similaire.

b) Selon les indications de la publication, la réduction électrochimique du CO₂ est-elle réalisable en l'absence de catalyseur et en quoi est-elle facilitée par le catalyseur ?

c) Le mode d'action du catalyseur est-il apparenté à un mécanisme par sphère externe ou interne ? Justifier.

d) Examinant le voltammogramme cyclique du composé **1** (courbe a de la fig.1), expliquer quelles transformations (nature du réactif et produit final) sont réalisées au niveau du 1^{er} et 2^{ème} pic de réduction (pics apparaissant respectivement à -1,56 et -1,80 V). Toujours, sur la courbe a de la fig. 1, à quelle transformation correspond le pic anodique situé à E_p = -0,51 V ?

Sous atmosphère de CO₂ et après addition de 5% de H₂O, la courbe a évolue vers la courbe c.

e) Quel est l'aspect particulier de la courbe c qui révèle la réduction de CO₂ par effet catalytique ? Quelle en est l'espèce active ?

Dans cet article sont également décrites des expériences d'électrolyse.

f) En quel produit le CO₂ est-il réduit ?

g) Par quelle grandeur l'efficacité du catalyseur est-elle représentée ?

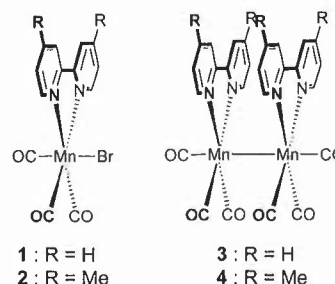
h) La réduction du CO₂ à l'électrode est-elle complètement sélective ? Justifier.

[Mn(bipyridyl)(CO)₃Br]: An Abundant Metal Carbonyl Complex as Efficient Electrocatalyst for CO₂ Reduction**

Marc Bourrez, Florian Molton, Sylvie Chardon-Noblat,* and Alain Deronzier*

Decrease of the massive amount of carbon dioxide that is released into the atmosphere is of vital importance for the environment. In complement or in parallel to the sequestration and storage of this greenhouse gas its chemical transformation into valuable organics and fuels could prove a potential answer to the CO₂ issues and also to the shortage of fossil fuels.^[1] However, the transformation of CO₂ requires a large amount of energy because CO₂ has the most oxidized state of carbon. Among various possible methods to “sustainably” transform CO₂, efficient and selective electrochemical reduction appears to be important and promising. This route may produce carbon-based fuels and chemicals utilizing CO₂ as an unlimited, cheap, and nontoxic renewable carbon source.^[2] The electrochemically driven reaction can be accomplished at bulk metallic electrodes, however it needs large overpotentials. Electrode poisoning often occurs and the selectivity is generally poor.^[3] These problems can be addressed by using molecular catalysts. Metal complexes are good candidates because their reduction is accompanied by the appearance of a vacant coordination site which is able to bind CO₂ and thus activate its reduction in the metal coordination sphere.^[4] Numerous metal complexes have been shown to be active electrocatalysts^[5]

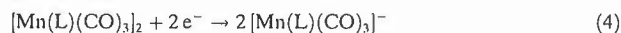
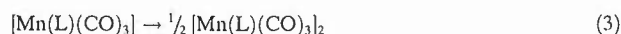
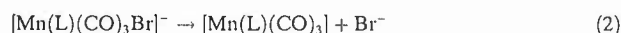
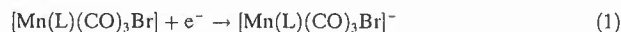
Herein, we demonstrate for the first time that [Mn(L)(CO)₃Br] complexes (**1**: L = 2,2'-bipyridine (bpy); **2**: L = 4,4'-dimethyl-2,2'-bipyridine (dmbpy); Scheme 1), syn-



Scheme 1. Chemical structures of the manganese carbonyl complexes.

thesized according to a known procedure,^[13] exhibit an excellent efficiency, selectivity, and stability for reducing CO₂ to CO, and the process occurs at a moderate overpotential.

The electrochemical behavior of **1** and **2** in MeCN with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) are similar to that previously reported for **1** in tetrahydrofuran (THF) electrolyte.^[12b] On the initial reduction scan, both Mn complexes undergo two successive irreversible reduction reactions (Figure 1a and Figures S1a (**1**) and S2a (**2**) in the Supporting Information) corresponding to the respective formation of the dimer [Mn(L)(CO)₃]₂ and the mononuclear [Mn(L)(CO)₃]⁻. Equations (1)–(4) summarize the probable mechanism. The formation of dimers has already been shown for **1** by IR and UV/Vis spectroelectrochemical experiments in THF electrolyte.^[12b]



A third reversible redox system not discussed here is also observed (Figure 1a). All potential values measured by cyclic voltammetry (CV) are reported in Table 1.

One-electron reduction reactions of **1** and **2** at -1.65 and -1.70 V, respectively, (Figures S1b and S2b in the Supporting Information) result in exhaustive formation of soluble dimers

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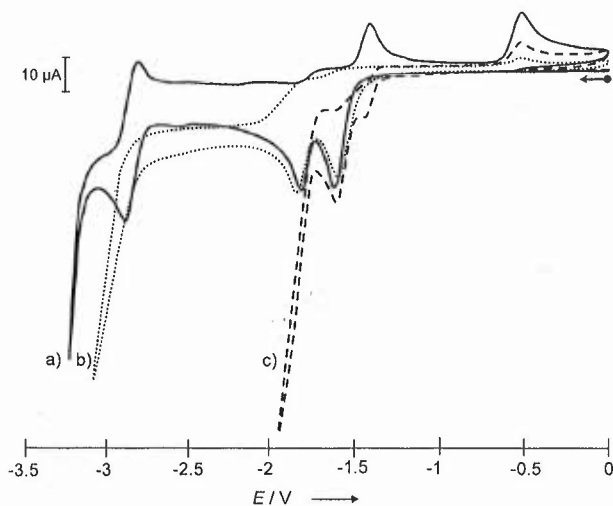
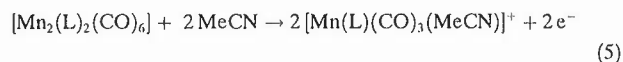


Figure 1. CVs of **1** at a concentration of 1 mM in MeCN with 0.1 M TBAP versus a vitreous carbon electrode of 3 mm diameter, $\nu = 100 \text{ mVs}^{-1}$ at room temperature a) under Ar and under CO_2 , b) without and c) with 5% of H_2O .

$[\text{Mn}(\text{L})(\text{CO})_3]_2$ (**3**: L = bpy; **4**: L = dmbpy; Scheme 1). UV/Vis spectra recorded during the bulk reductive electrolysis in MeCN (insets of Figures S1 and S2 in the Supporting Information) show the progressive growth of characteristic and intense absorption bands of $[\text{Mn}(\text{L})(\text{CO})_3]_2$ species in good agreement with those previously reported for the electro-^[12b] and photo-^[14] generated dimer **3** in THF.

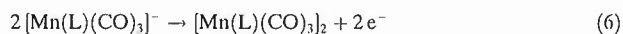
The dimers show in turn an irreversible two-electron oxidation leading to the corresponding acetonitrile monomer complexes $[\text{Mn}(\text{L})(\text{CO})_3(\text{MeCN})]^+$ (Table 1; Figures S1b and S2b in the Supporting Information; [Eq. (5)]). On the reverse scan new reduction peaks are located at around 150 mV before the potential where $[\text{Mn}(\text{L})(\text{CO})_3\text{Br}]$ species are

reduced. These new peaks are attributed to the reduction of the solvent-coordinated complexes $[\text{Mn}(\text{L})(\text{CO})_3(\text{MeCN})]^+$ formed during the oxidation processes.



The electrogeneration of Mn acetonitrile complexes has been proved by comparison of the spectroscopic and electrochemical properties (Table 1) of the electrolyte solutions obtained after exhaustive two-electron oxidation of dimers **3** and **4** with those of the two authentic samples of $[\text{Mn}(\text{L})(\text{CO})_3(\text{MeCN})](\text{PF}_6)$ (L = bpy and dmbpy), synthesized following an adapted literature procedure (see the Supporting Information).^[16]

Exhaustive electrochemical formation of $[\text{Mn}(\text{L})(\text{CO})_3]^-$ (second irreversible reduction process of **1** and **2**) has been also evidenced by in situ UV/Vis spectroscopy. During the bulk reduction reactions of **3** and **4** new intense bands appear in the visible range (around 560 nm; Table 1) which are in agreement with those observed in THF.^[12b, 17] However, these anionic species are moderately stable (see Figures S3 and S4 in the Supporting Information). The $[\text{Mn}(\text{L})(\text{CO})_3]^-$ species are oxidized at less negative potentials (around 0.40 V) than those of the parent dimer reduction reactions and lead mainly to the recovery of the dimers [Eq. (6)].



When an acetonitrile solution of **1** is saturated with CO_2 (Figure 1b) no significant difference is observed in the first two reduction peaks, while the addition of H_2O induces a dramatic change (Figure 1c) with a strong enhancement of the cathodic current at the second reduction system [Eq. (4)]. This indicates the involvement of the reduced Mn dimer as the active species in the electrocatalytic process. In addition, with the presence of water under CO_2 , a new reduction peak appears at a potential that is 150 mV less negative than the first reduction peak of **1** (Figure 1c). This peak is attributed to the reduction of $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{S})]^+$ (S = MeCN or/and H_2O) resulting from partial solvolysis of **1**. This has been confirmed by analysis of UV/Vis absorption spectra and CV evolutions under Ar of an acetonitrile solution of **1** containing 5% of slightly acidified H_2O (pH 4), which mimics the acidity

effect brought about by CO_2 (see Figures S5 and S6 in the Supporting Information). The fact that water is needed to obtain a significant catalytic activity is consistent with the activity observed with other electrocatalysts based on metal carbonyl complexes.^[7, 9, 18] In the case of rhenium it has been reported that the addition of a weak Brønsted acid, including water, stabilizes the rhenium-carbon dioxide intermediate most likely through protonation and thus facilitates the cleavage of one of the C–O bonds of CO_2 to

Table 1: Redox potentials^[a] and UV/Vis data of manganese carbonyl complexes in MeCN with 0.1 M TBAP.

Complexes	$E(\text{Red}_1)$ [V] ^[b]	$E(\text{Ox})$ [V] ^[b]	$E(\text{Red}_2)$ [V] ^[b]	λ [nm]
$[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ (1)	−1.56	−	−1.80	366 (sh), 416
$[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^{[c]}$	−1.42	−	−1.80	376
$[\text{Mn}(\text{dmbpy})(\text{CO})_3\text{Br}]$ (2)	−1.64	−	−1.89	360 (sh), 412
$[\text{Mn}(\text{dmbpy})(\text{CO})_3(\text{MeCN})]^{[c]}$	−1.50	−	−1.89	375
$[\text{Mn}(\text{bpy})(\text{CO})_3]_2$ (3)	−1.80	−0.51	−	394, 461, 633, 806
$[\text{Mn}(\text{bpy})(\text{CO})_3]^-$	−	−1.39	−	370, 560, 626 (sh)
$[\text{Mn}(\text{dmbpy})(\text{CO})_3]_2$ (4)	−1.89	−0.59	−	404, 445, 538 (sh), 638, 817
$[\text{Mn}(\text{dmbpy})(\text{CO})_3]^-$	−	−1.48	−	374, 561

[a] Determined by CV ($\nu = 100 \text{ mVs}^{-1}$); Mn complexes of around 1 mM; CV disk working electrode (diameter of 3 mm) and 10 mM Ag/Ag^+ reference electrode. [b] Successive cathodic (Red₁) and anodic (Ox) peak potentials of redox systems. [c] Synthesized complexes.

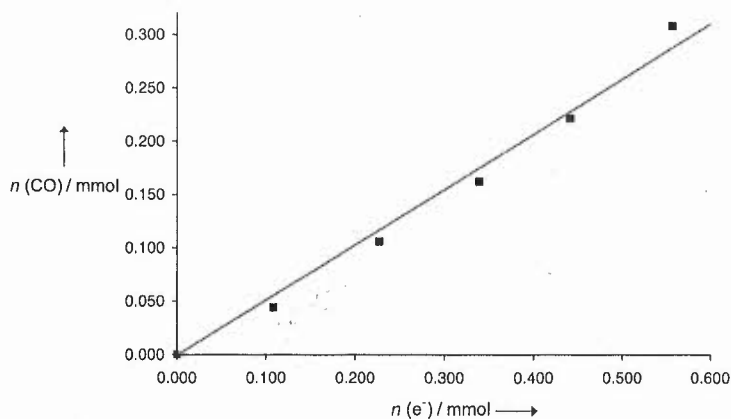


Figure 2. Number of CO moles produced during the reduction of CO₂ at -1.70 V in MeCN with 0.1 M TBAP and 5% H₂O under CO₂ containing 2.5×10^{-2} mmol of **1** versus the number of electrons consumed.

yield CO.^[19] A similar situation was previously reported by Saveant and co-workers for the electrocatalytic reduction of CO₂ with iron porphyrin.^[20] Some complementary experiments will be done with Mn complexes to precisely determine the mechanism of the electrocatalytic process.

To confirm the catalytic activity of **1** and to determine the selectivity of the CO₂ reduction we have carried out preparative-scale electrolysis. Controlled potential electrolysis at -1.70 V (the foot of the catalytic reduction peak) of a solution containing the complex at a concentration of 1 mM in MeCN/H₂O (95/5) under CO₂, which was followed by gas chromatography (GC). The product analysis shows that the amount of CO produced is directly proportional to the number of consumed electrons (Figure 2; turnover number: TON = 13 for 4 h).

For an electrolysis time of 4 h there is a quantitative Faradic efficiency for production of CO without generation of hydrogen. Because of the formation of electrocatalytic species the current density decreases at first during the consumption of the first 0.1 mmole of electrons (0.5 h) and then is perfectly stable (0.2 mA cm⁻²) for a further 3.5 h, indicating that the concentration of electrogenerated catalytic intermediates remains stable in solution. After 4 h of electrolysis we have confirmed by CV that **1** is totally stable. However, after longer electrolysis times at -1.70 V the current starts to decrease (0.07 mA cm⁻² h⁻¹) until it reaches a perfectly stable value (0.06 mA cm⁻²). Finally, after 22 h ($Q = 130$ C) CO production ($\rho = 85\%$) is associated with H₂ production ($\rho = 15\%$).

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