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Dancheng Chen, Paul-Louis Fabre, Olivier Reynes, Nadia Chouini-Lalanne, Valérie Sartor. Electrocarboxylation of chloroacetonitrile mediated by a Ni(I) terpyridine complex: Voltammetric and spectroscopic studies. *Inorganica Chimica Acta*, 2021, 524, pp.120442. 10.1016/j.ica.2021.120442 . hal-03270705

HAL Id: hal-03270705

<https://hal.science/hal-03270705v1>

Submitted on 24 May 2023

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Electrocarboxylation of chloroacetonitrile mediated by a Ni(I) terpyridine complex: voltammetric and spectroscopic studies

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Abstract: Cyclic voltammetry and spectroelectrochemistry (e.p.r.) were used to investigate the mechanisms implied in the electrocarboxylation of chloroacetonitrile (Cl-CH₂-CN, noted RCl) mediated by [Ni(II)(terpy)₂]²⁺. The oxidative addition of chloroacetonitrile on the electrogenerated [Ni(I)(terpy)]⁺ yields an alkyl-nickel R-Ni(III) complex which is reduced into an alkyl-nickel(II). E.p.r study shows that the homolytic nickel-carbon bond cleavage seems to be the more probable pathway to form the organic radical R[•], which is reduced to R⁻. Under carbon dioxide atmosphere, cyclic voltammetry studies show that CO₂ was added on the alkyl-Ni(III) complex giving probably a CO₂ adduct which is reduced to RCO₂-Ni(II) complex allowing to release the carboxylate RCO₂⁻ and the active [Ni(I)(terpy)]⁺ complex.

Controlled potential electrolyses showed that good carboxylated and faradic yields were obtained.

Keywords: Electrocatalysis, Nickel bis(terpyridine) complex, carbon dioxide, chloroacetonitrile, cyanoacetic acid, spectroelectrochemistry.

1. Introduction

In order to valorise carbon dioxide which is an abundant and relatively inexpensive waste, the electrocarboxylation of alkyl halides (RX) into carboxylated products (R-COO⁻) has been extensively studied [1-5]. Among all the electrocarboxylation methods, the direct electroreduction of alkyl halides under carbon dioxide atmosphere at various metallic electrodes has been studied. High faradic yields were obtained but required highly negative working potentials associated to passivation phenomena [6, 7]. However, due to the specific reactivity of silver towards halides, when a silver electrode was used at cathode, good faradic yields were obtained with a low working potential [8]. On the other hand, it is confirmed that the use of catalytic systems based on transition-metal complex is also an efficient pathway for the electrocarboxylation of alkyl halides. Several nickel [9-11], palladium [12] and cobalt [13-15] complexes have been reported to prepare carboxylated products. Carboxylation of chloroacetonitrile (Cl-CH₂-CN) has received much attention due to the relevant interest of the resulting cyanoacetic acid which is used in many industrial processes [16, 17]. Actually, the chemical preparation of cyanoacetic acid is particularly environmentally unfriendly and toxic [18]. In order to develop a safer process, the electrocarboxylation of chloroacetonitrile using nickel [19] and cobalt [20, 21] complexes have been studied. The best result was been obtained with the Ni(salen) planar complex

giving the cyanoacetic acid with a yield of 71 % under an applied potential of -1.7 V/SCE [19]. The catalytic processes go through the oxidative addition of the alkyl halide on the metallic centre and require at least one free coordination site on the metal. Recently, full coordinated Co(II) complexes have also shown interesting properties toward electrocarboxylation of chloroacetonitrile due to the loss of a ligand allowing the oxidative addition of alkyl halide [20, 21]. Considering these works, many full coordinated transition-metal complexes, which have never been studied before, can show interesting catalytic properties to give cyanoacetic acid.

We report, in this paper, the electrocatalytic properties of hexacoordinated $[\text{Ni}(\text{II})(\text{terpy})_2]^{2+}$ complex for the electrocarboxylation of chloroacetonitrile $\text{Cl-CH}_2\text{-CN}$. The overall process is studied by cyclic voltammetry and spectroelectrochemical experiments in order to propose a catalytic cycle. Studies were conducted under argon and carbon dioxide atmospheres. The influence of the applied potential on the faradic and carboxylated yields were studied through bulk electrolyses.

2. Materials and methods

2.1 Reagents and synthesis

Acetonitrile (HPLC grade), used as solvent, was stored on molecular sieves (3 Å). Tetrabutylammonium hexafluorophosphate (TBAPF_6), used as support salt, was recrystallized from ethyl acetate and dried at 80 °C under vacuum. 2,2':6',2''-Terpyridine, nickel (II) chloride hexahydrated, chloroacetonitrile, cyanoacetic acid, succinonitrile and potassium hexafluorophosphate (KPF_6) were used as received. The $[\text{Ni}(\text{terpy})_2]\text{Cl}_2$, synthesized as described in literature [22], was converted to its corresponding hexafluorophosphate salt by metathesis with KPF_6 . The resulting complex was dissolved in

dry acetonitrile and crystals of $[\text{Ni}(\text{terpy})_2](\text{PF}_6)_2$ were grown by low diffusion of diethyl ether into acetonitrile solution.

2.2 Instrumentations

Voltammetric experiments were conducted in a three-electrode cell in dry acetonitrile + TBAPF_6 0.1 mol.L^{-1} under argon or carbon dioxide atmospheres at room temperature by using an Autolab 20 potentiostat (EcoChemie). The working electrode was a glassy carbon disc (diameter 3 mm). The reference electrode was a saturated calomel electrode (S.C.E) equipped with a double junction. The counter electrode was a platinum wire. Controlled potential electrolyses were carried out as previously described [20]. The cyanoacetic acid was extracted using the procedure previously reported [19]. In order to identify and quantify cyanoacetic acid formed during electrolysis, standard solutions of commercial cyanoacetic acid were previously analysed by HPLC using a HP 1100 HPLC equipped with a UV-Vis detector operating at 200 nm and a Sugar SH1011 column eluted by $5 \cdot 10^{-3} \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$.

For e.p.r. spectroelectrochemical experiments, a Bruker EMX-8/2.7 (9.86 GHz) equipped with a high-sensitivity cavity (4119/HS 0205) and a gaussmeter (Bruker, Wissembourg, France) was used for the analysis of radicals trapped by PBN. PBN, N-tert-butyl- α -phenylnitrone, is a spin trap already used for the detection of radicals during photolysis experiments of alkylcobaloximes [23]. Two types of measurements were carried out:

(i) In the e.p.r. flat quartz cell the electrolysis ($E_{\text{applied}} = -1.2 \text{ V}$) of $[\text{Ni}(\text{terpy})_2]^{2+} 2 \cdot 10^{-3} \text{ mol.L}^{-1}$ in presence of chloroacetonitrile $10^{-2} \text{ mol.L}^{-1}$ and PBN $10^{-2} \text{ mol.L}^{-1}$ was achieved in order to study the R-Ni(II) cleavage. The e.p.r. spectra were recorded during the electrolysis.

(ii) The study of the R-Ni(II) cleavage required a separate electrolysis ($E_{\text{applied}} = -1.2$ V) of $[\text{Ni}(\text{terpy})_2]^{2+}$, 2.10^{-3} mol.L $^{-1}$. After exhaustive electrolysis, a green solution is obtained and 0.01 mol.L $^{-1}$ of chloroacetonitrile was added; the solution turned red. After addition of PBN 10^{-2} mol.L $^{-1}$, the e.p.r. spectra were recorded.

3. Results and discussion

3.1 Activation of chloroacetonitrile under argon atmosphere

As already described, $[\text{Ni}^{\text{II}}(\text{terpy})_2]^{2+}$ complex exhibits four electronic transfers in the cathodic domain $[-2$ V ; 0 V] under an argon atmosphere in acetonitrile (figure I, curve 1) [24 - 27].

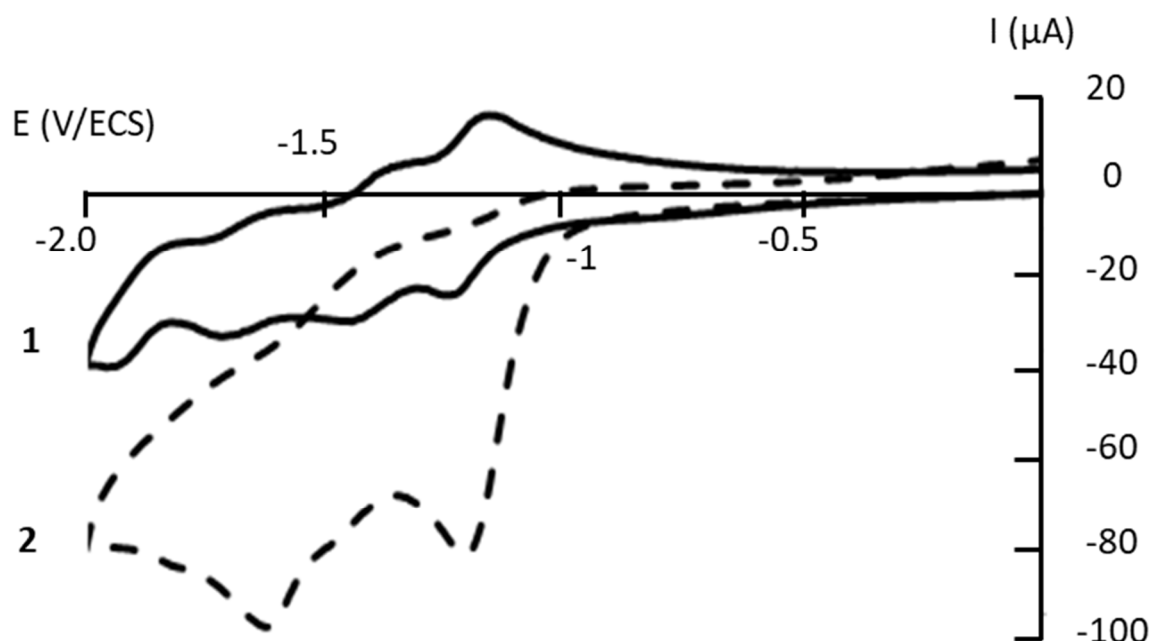
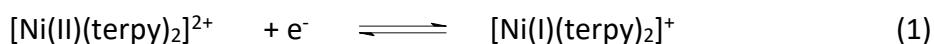


FIGURE I: Cyclic voltammograms, recorded at a GC electrode under argon, in $\text{CH}_3\text{CN} + \text{TBAPF}_6$. $v = 100$ mV/s. (1, —) 1 mmol.L $^{-1}$ $[\text{Ni}(\text{II})(\text{terpy})_2]^{2+}$, (2, - -) 1 mmol.L $^{-1}$ $[\text{Ni}(\text{II})(\text{terpy})_2]^{2+}$ and 2 mmol.L $^{-1}$ chloroacetonitrile.

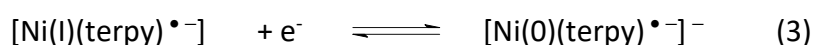
At $E_1 = -1.25$ V, the mono-electronic reversible reduction of metallic centre is observed.



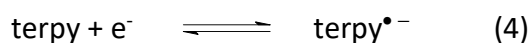
The second electrochemical system observed at $E_2 = -1.45$ V, corresponds to the reduction of terpyridine ligand associated to the loss of a terpyridine ligand.



The third reduction at $E_3 = -1.72$ V is due to the reduction of Ni(I) metallic center to form the neutral Ni(0) complex.



The last reduction which is irreversible at $E_4 = -1.95$ V corresponds to the reduction of free terpyridine ligand release during reaction (2).



In presence of increasing amounts of chloroacetonitrile ($\text{Cl-CH}_2\text{-CN}$, noted RCl) under argon atmosphere, the voltammogram of $[\text{Ni(II)(terpy)}_2]^{2+}$, drawn until -2 V, was strongly modified (Figure I, curve 2). The anodic backward peaks observed for the three first reductions disappeared. Associated to the loss of reversibility, an increase in the cathodic forward peak was observed. These observations show the reactivity between the electrogenerated complexes, obtained from reactions (1) to (3), and chloroacetonitrile and the activation of RCl by Ni(II)/Ni(I) redox couple.

For the sake of clarity, the report is restricted to the first mono-electronic reduction of $[\text{Ni}^{\text{II}}(\text{terpy})_2]^{2+}$ (figure II).

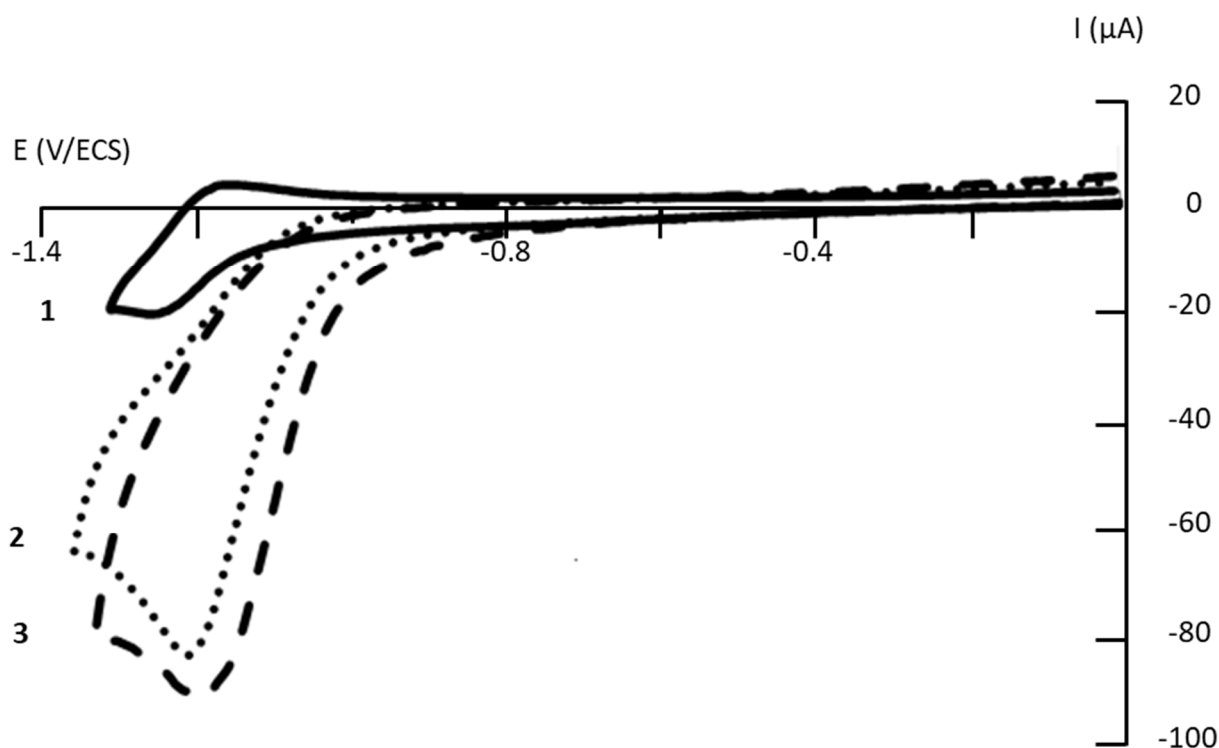
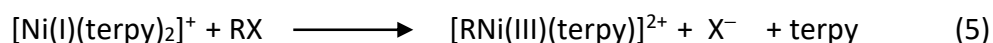


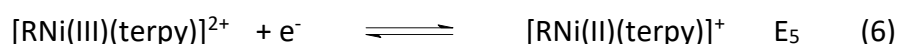
FIGURE II: Cyclic voltammograms, recorded at a GC electrode under argon, in $\text{CH}_3\text{CN} + \text{TBAPF}_6$. $v = 100 \text{ mV/s}$. (1, —) $1 \text{ mmol.L}^{-1} [\text{Ni(II)(terpy)}_2]^{2+}$, (2, ••••) $1 \text{ mmol.L}^{-1} [\text{Ni(II)(terpy)}_2]^{2+}$ and 2 mmol.L^{-1} chloroacetonitrile, (3, — —) $1 \text{ mmol.L}^{-1} [\text{Ni(II)(terpy)}_2]^{2+}$ and 5 mmol.L^{-1} chloroacetonitrile.

In presence of chloroacetonitrile, the mono-electronic reversible reduction of Ni(II)/Ni(I) redox couple was modified (figure II). The anodic backward peak disappeared showing a chemical reaction associated to the electrogenerated $[\text{Ni(I)(terpy)}_2]^+$. This behaviour is typical of an EC scheme due to the oxidative addition of RX on electrogenerated Ni(I) complex to give an organo-nickel(III) complex (reaction 1 and 5) [28-30]. For the electrogenerated $[\text{Ni(I)(terpy)}_2]^+$ complex, the oxidative addition of chloroacetonitrile implies the release of a terpyridine ligand to form the undercoordinated $[\text{Ni(I)(terpy)}]^+$ complex as already described for hexacoordinated cobalt complexes [21, 31].

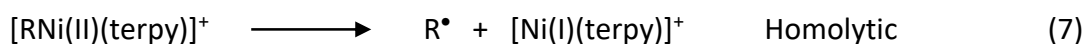


Associated to the loss of reversibility, when the concentration of chloroacetonitrile increases, the cathodic peak rises to 5 molar equivalents of RX. Moreover, the potential cathodic peak shifts to less negative potentials ($E_{p,c} = -1,2 \text{ V}$) when the scan rate was increased and no reverse oxidation peak was observed.

This behaviour shows that the oxidative addition, reaction (5) - EC scheme, is coupled with another reaction. The increase in cathodic currents in presence of chloroacetonitrile at low scan rate is too high for a simple EC scheme. These observations show a second electronic transfer corresponding to the reduction of the organo-nickel complex at a less negative potential compared to Ni(II)/Ni(I) complex.



Recently, many works have shown that the Nickel-Alkyl complexes, synthesized chemically, were stable and have been isolated [28-31]. However, others works have shown that the electrogenerated alkyl-nickel(II) complexes, coming from the reduction of alkyl-nickel(III) complex, are generally unstable [32, 34, 36], and underwent a rapid homolytic (7) or heterolytic (8) Ni-R bond cleavage.



In order to investigate what is the favourable cleavage of alkyl-Ni(II) complex, e.p.r spectroscopies were carried out. The complex R-Ni(II) was synthesized by exhaustive electrolysis of a solution of CH₃CN + 0.1 mol.L⁻¹ TBAPF₆ containing the complex Ni(terpy)₂(PF₆)₂ (2.10⁻³ mol.L⁻¹) at -1,2 V to electrogenerate the [Ni(I)(terpy)]⁺ complex in presence of 10⁻² mol.L⁻¹ of chloroacetonitrile and the spin trap PBN (10⁻² mol.L⁻¹). The e.p.r. spectrum of the solution shows a signal corresponding to the R-PBN[•] radical: a triplet characterized by the hyperfine constants a_N = 13.4 G, corresponding to the coupling of the electron spin with the core spin of the PBN nitrogen atom associated to the nuclear spin of the PBN hydrogen (a_H = 1.7 G) which splits the triplet further into doublets (figure III). The signal intensity of R-PBN[•] radical was weak showing that the dissociation was slow.

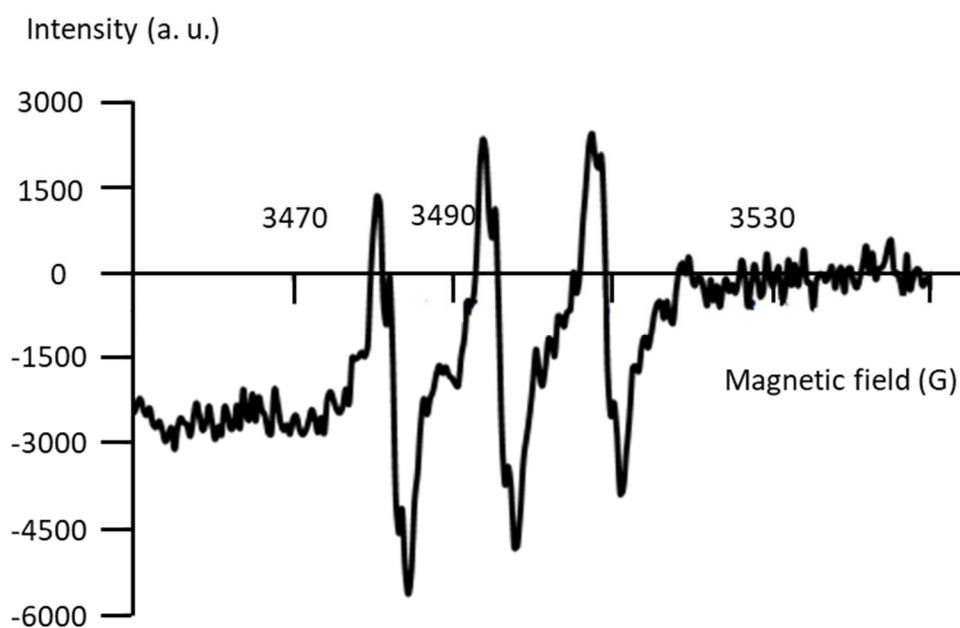
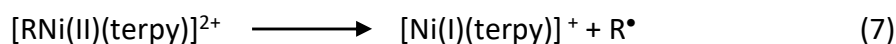


FIGURE III: *e.p.r* spectrum of a solution containing the electrogenerated [Ni(terpy)₂]⁺ (2.10⁻³ mol/L) in the presence of chloroacetonitrile 10⁻² mol/L and the spin trap PBN 10⁻² mol/L.

The e.p.r. experiment shows that the homolytic Ni-R bond cleavage of $[\text{RNi(II)(terpy)}]^+$ complex seems to be the more probable pathway (7) to give the $[\text{Ni(I)(terpy)}]^{2+}$ complex and organic radical R^\bullet . Note that the heterolytic alkyl-Ni(II) bond cleavage cannot be totally excluded.

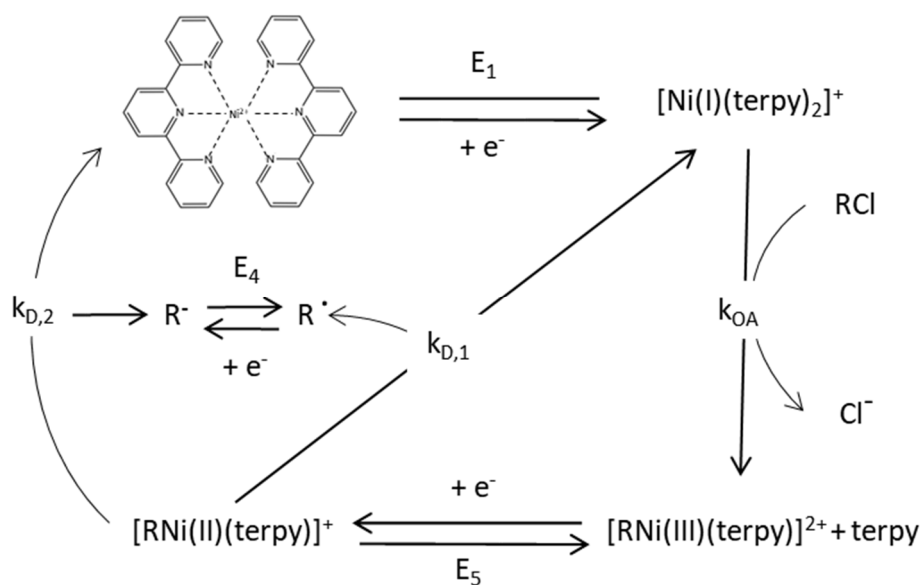


Through reaction (5), the electrochemical process presents the characteristics of an E_c catalytic behaviour which explains the increase in the cathodic peak current under low potential scan rate. The homolytic dissociation of the alkyl-nickel(II) (7) gives the $[\text{Ni(I)(terpy)}]^+$ complex which then turns in a new catalytic cycle. The radical R^\bullet is then reduced to R^- ($\text{NC-CH}_2^\bullet/\text{NC-CH}_2^-$ $E^\circ = -0.69 \text{ V versus SCE}$ [35]). The resulting carbanion R^- can then react with chloroacetonitrile via a selfprotonation reaction or with electrophilic species [38].

Whatever the cleavage, the global electron exchange is bielectronic and catalytic. Indeed, after the reduction of the alkyl-nickel(III) (6),

- Either the radical R^\bullet coming from the homolytic Ni-R bond cleavage (7) was reduced into R^-
- Or the reduction of $[\text{Ni(II)(terpy)}]^{2+}$ into $[\text{Ni(I)(terpy)}]^+$ coming from the heterolytic Ni-R bond cleavage (8) was observed.

The cyclic voltammetry and spectroelectrochemical studies show that the activation of chloroacetonitrile can be described by scheme 1.



Scheme: Mechanisms implied in electrocatalytic properties of $[\text{Ni}(\text{II})(\text{terpy})_2]^{2+}$ under argon atmosphere.

The oxidative addition of RCl (scheme 1, k_{OA} : oxidative addition kinetic constant) on the electrogenerated Ni(I) complex, associated to the loss of a terpyridine ligand, yields an alkylcobalt complex $[\text{R-Ni}(\text{III})(\text{terpy})]^{2+}$ which is reduced into the unstable $[\text{R-Ni}(\text{II})(\text{terpy})]^+$ complex (scheme 1, E_5). The reduced complex $[\text{RNi}(\text{II})(\text{terpy})]^+$ decomposes rapidly, probably in an homolytic process (scheme 1, $k_{\text{D}1}$: dissociation kinetic constant), as suggested by e.p.r. study, to give radical R^\bullet which is then reduced into R^- at the potentials where the reduction of $[\text{RNi}(\text{III})(\text{terpy})]^{2+}$ is observed (scheme 1, E_5). Note that the heterolytic the bond cleavage of nickel-carbon (scheme 1, $k_{\text{D}2}$: dissociation kinetic constant) cannot be totally exclude during catalytic process. Whatever the homolytic or heterolytic dissociation, due to redox potentials of $\text{NC-CH}_2^\bullet/\text{NC-CH}_2^-$ and $[\text{Ni}(\text{II})(\text{terpy})]^{2+}/[\text{Ni}(\text{I})(\text{terpy})]^+$, the yielded products were R^- and $[\text{Ni}(\text{I})(\text{terpy})]^+$.

3.2 Activation of chloroacetonitrile under carbon dioxide atmosphere

Figure IV shows the voltammograms recorded in a CO₂-saturated solution.

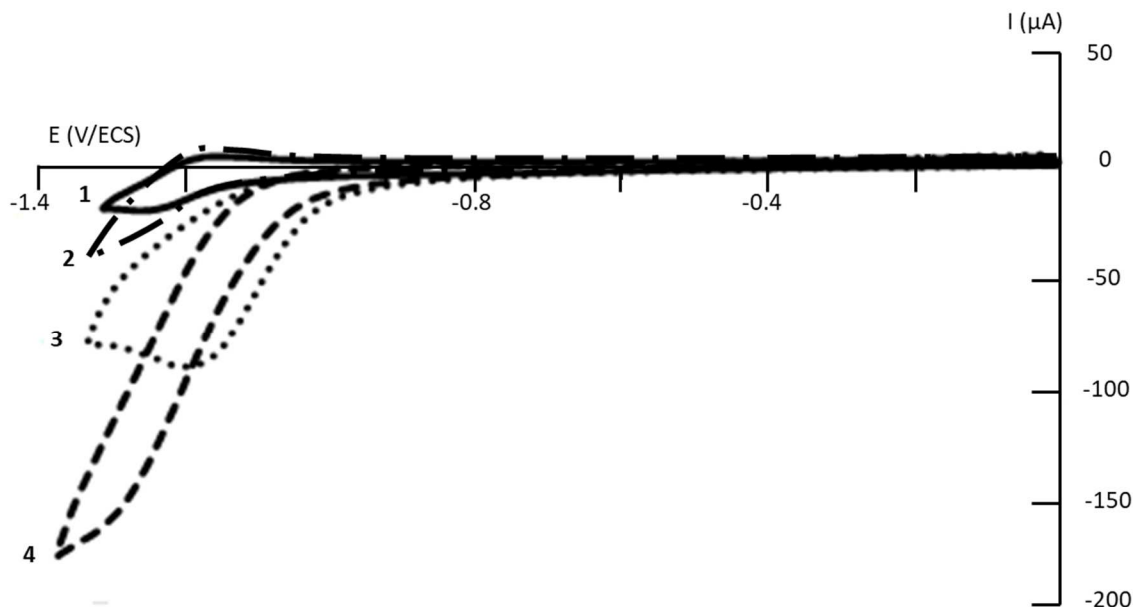


FIGURE IV: Cyclic voltammograms, recorded at a GC electrode in CH₃CN + TBAPF₆. $v = 100$ mV/s. (1, —) 10^{-3} mol/L [Ni(II)(terpy)₂]²⁺ under argon; (2, — • —) 10^{-3} mol/L [Ni(II)(terpy)₂]²⁺ in a CO₂-saturated solution; (3, • • • •) 10^{-3} mol/L [Ni(II)(terpy)₂]²⁺ and $5 \cdot 10^{-3}$ mol/L chloroacetonitrile under argon; (4, — —) 10^{-3} mol/L [Ni(II)(terpy)₂]²⁺ and $5 \cdot 10^{-3}$ mol/L chloroacetonitrile in a CO₂-saturated solution.

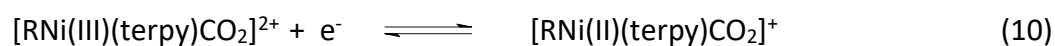
The voltammogram of [Ni(II)(terpy)₂]²⁺ complex under CO₂ (curve 2) is modified compared to under argon atmosphere (curve 1) showing that the electrogenerated Ni(I) complex reacts with CO₂, as already described [39]. Curve 3 corresponds to the voltammogram of [Ni(II)(terpy)₂]²⁺ complex in the presence of five-fold excess of chloroacetonitrile under an argon atmosphere. As described above, it corresponds to the chloroacetonitrile activation. Curve 4 shows the voltammogram of [Ni(II)(terpy)₂]²⁺ complex with five-fold excess of chloroacetonitrile under CO₂. By comparison with the curves 2 and 3,

the intensity of the cathodic peak is strongly enhanced under carbon dioxide atmosphere in presence of chloroacetonitrile and the forward potential peak shifts to more cathodic potential ($E_{p,c} = -1.3$ V) compared to -1.2 V observed under argon atmosphere with chloroacetonitrile. These observations imply that carbon dioxide enters the catalytic cycle and interferes in the reduction cycle of chloroacetonitrile [20].

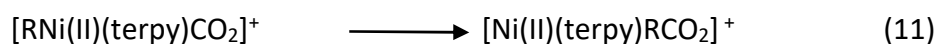
Moreover, under CO_2 -atmosphere, the mono-electronic reduction of $[\text{RNi(III)(terpy)}]^{2+}$ complex is not observed and the shift of forward peak potential indicates that another complex is implied in the catalytic cycle. Taking into account, the behaviour of Ni or Pd complexes used as catalysts for electrocarboxylation [10, 12], it seems reasonable to assume that CO_2 was added on R-Ni(III) complex.



The carboxylated complex is then reduced to $[\text{RNi(II)(terpy)CO}_2]^+$ at a more cathodic potential (reaction 10) compared to the potential reduction of $[\text{RNi(III)(terpy)}]^{2+}$.



After addition of CO_2 (9) and reduction of alkyl carboxylated Ni(III) complex (10), it was assumed that the carboxylated complex $[\text{RNi(II)(terpy)CO}_2]^+$ underwent a coupling (11) between alkyl R and CO_2 to give, after dissociation, the carboxylate anion RCO_2^- and the undercoordinated complex $[\text{Ni(II)(terpy)}]^{2+}$.



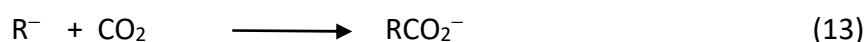
The peak current ($E_{p,c} = -1.3$ V) is not related to square root of scan rate. When the scan rate increases, the current peak normalized to square root of scan rate decreases showing that a chemical reaction limits the process. Taking into account the high concentration of carbon dioxide ($[\text{CO}_2] = 0.28 \text{ mol.L}^{-1}$ in CO_2 -saturated solution [35]), the reaction (9) must be

favoured. It is assumed that the limiting reaction is the dissociation of $[\text{Ni(II)(terpy)RCO}_2]^+$ (11).

The overall activation of CO_2 was:



Note that the carbanion R^- [40] yielded from the chloroacetonitrile activation can also react directly with CO_2 (13):



The spectroscopic and voltammetric studies show that $[\text{Ni(II)(terpy)}_2]^{2+}$ complex is a good candidate for the electrocarboxylation of chloroacetonitrile into cyanoacetic acid.

3.3 Bulk Electrolyses

In order to quantify the products formed, preparative electrolyses at different applied potentials were carried out in CO_2 -saturated solution in the presence of chloroacetonitrile (ten-fold excess) and nickel complex. The faradic and carboxylated yields obtained for different electrolysis potential are summarized in table I. Note that acetonitrile formed during electrolysis cannot be determined.

Table I. Electrocarboxylation of chloroacetonitrile in acetonitrile + 0.1 mol.L⁻¹ TBAPF₆ solution^a

Entry	E ^b (V)	Charge passed (C)	RCO ₂ H (%) ^c	Faradic yield (%) ^d
1	-1.2	50	37 ± 1 %	37 ± 1 %
2	-1.3	60	53 ± 0.5 %	50 ± 0.5 %
3	-1.4	80	61 ± 1 %	61 ± 1 %
4 ^e	-1.2	22	0 %	0 ± 1 %

^a Electrolyses were performed in an undivided cell at room temperature in the presence of 10^{-2} mol.L⁻¹ and Cl-CH₂-CN 10^{-3} mol.L⁻¹ of [Ni(II)(terpy)₂](PF₆)₂. The electrolytic solution was saturated with CO₂. The theoretical charge is 48 C for the total conversion of the substrate in a 2 e⁻ process.

^b Electrolysis potential *versus* S.C.E.

^c Calculated as $N_{\text{RCOOH}}/N_{\text{RCl}}$.

^d Calculated as $f = Q_{\text{RCOOH}}/Q_{\text{passed}}$. Where $Q_{\text{RCOOH}} = 2 F N_{\text{RCOOH}}$ (N_{RCOOH} is the number of moles of cyanoacetic produced by electrolysis) and Q_{passed} is the measured electric charge.

^e Without Cl-CH₂-CN.

Good faradic and carboxylated yields (around 50 - 60 %) obtained for applied potential to -1.3 V and -1.4 V show the interesting electrocatalytic properties of complex. Compared to Ni(salen) complex [19], the carboxylate yields were lower. However, the over potential is much lower, about 0.4 V. When the electrolysis potentials were smaller than -1.3 V, the faradic and carboxylated yields decrease dramatically to 37 %. These results are in accordance with voltammetric studies. Indeed in the potential range [-1.3 ; -1.4 V], [RNi(III)(terpy)CO₂]²⁺ complex is reduced to [RNi(II)(terpy)CO₂]⁺ which is unstable and gives RCO₂⁻ and [Ni(II)(terpy)]²⁺. In this range of potential, Ni(II) complex is then reduced to Ni(I) complex which can react with RCl and CO₂ to form [RNi(III)(terpy)CO₂]²⁺ complex. The faradic yields never reach 100%. This limitation of faradic yield is due to competition between the reduction of [RNi(III)(terpy)]²⁺ and the formation of [RNi(III)(terpy)CO₂]²⁺. Cyclic voltammetry and e.p.r studies show that the [RNi(III)(terpy)]²⁺ complex reduction to [RNi(II)(terpy)]⁺ gives radical R[•] which either dimerizes to give the assumed dimer R-R or is reduced to R⁻

carbanion which reacts either with CO₂ to give cyanoacetic acid or is deactivated by protonation to give acetonitrile. Note that succinonitrile, coming from the radical R[•] dimerization, is not detected in bulk electrolysis showing that the radical reduction is the preferential pathway.

The limitation of faradic yield is also due to the reactivity of electrogenerated [Ni(I)(terpy)₂]⁺ complex towards CO₂ [39]. In CO₂-saturated solution without chloroacetonitrile, at a -1.2 V applied potential, the charge passed (22 C) is higher than the theoretical charge (2,4 C) needs for the mono-electronic reduction of [Ni(II)(terpy)]²⁺ complex.

4. Conclusion

Electrochemical experiments have shown the oxidative addition of chloroacetonitrile onto the electrogenerated [Ni(I)(terpy)]⁺ active complex to give an alkyl-nickel(III) complex which is then reduced to [RNi(II)(terpy)]⁺. E.p.r experiments show that alkyl-nickel(II) complex undergoes a homolytic dissociation to liberate R[•] radical which is reduced to R⁻ carbanion and the active complex [Ni(I)(terpy)]⁺ which enters a new catalytic cycle. Under CO₂ atmosphere, it is assumed that the addition of carbon dioxide on [RNi(III)(terpy)]²⁺ results in a carboxylate complex which is reduced to more cathodic potential. The [Ni(II)(terpy)RCO₂]⁺ complex after dissociation gives the carboxylate anion RCO₂⁻.

Electrolysis experiments have shown that at an applied potential of -1.3 V and -1.4 V, the faradic yields in cyanoacetic acid were good (around 60%) with an overpotential much lower (0.4 V) than those applied for the electrocarboxylation mediated by Ni(salen) [19].

Acknowledgements

The authors would like to thank Pierre Perio (Laboratoire PHARMA-DEV, UMR IRD 152, Université de Toulouse) for his technical assistance in the e.p.r. experiments.

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