



## Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>  
Eprints ID: 5776

**To link to this article:** DOI:10.1016/J.ELECOM.2010.07.020  
URL: <http://dx.doi.org/10.1016/J.ELECOM.2010.07.020>

**To cite this version:** Fabre, Paul-Louis and Reynes, Olivier (2010) Electrocarboxylation of chloroacetonitrile mediated by electrogenerated cobalt(I) phenanthroline. *Electrochemistry Communications*, vol.12 (n°10). pp. 1360-1362. ISSN 1388-2481

Any correspondence concerning this service should be sent to the repository administrator: [staff-oatao@listes.diff.inp-toulouse.fr](mailto:staff-oatao@listes.diff.inp-toulouse.fr)

# Electrocarboxylation of chloroacetonitrile mediated by electrogenerated cobalt(I) phenanthroline

P.-L. Fabre, O. Reynes\*

Université de Toulouse, Université Paul Sabatier, Laboratoire de Génie Chimique, Bat. 2R1, 118 route de Narbonne, F-31062 Toulouse cedex 09, France  
CNRS, Laboratoire de Génie Chimique UMR 5503, F-31062 Toulouse cedex 09, France

## A B S T R A C T

The electrocarboxylation of chloroacetonitrile mediated by  $[\text{Co}(\text{II})(\text{phen})_3]^{2+}$  has been investigated. Cyclic voltammetry studies of  $[\text{Co}(\text{II})(\text{phen})_3]^{2+}$  have shown that  $[\text{Co}(\text{I})(\text{phen})_3]^+$ , an 18 electron complex, activates chloroacetonitrile by an oxidative addition through the loss of a phenanthroline ligand to give  $[\text{RCO}(\text{III})(\text{phen})_2\text{Cl}]^+$ . The unstable one-electron-reduced complex underwent Co–C bond cleavage. In carbon dioxide saturated solution,  $\text{CO}_2$  insertion proceeds after reduction of the alkylcobalt complex. A catalytic current is observed which corresponds to the electrocarboxylation of chloroacetonitrile into cyanoacetic acid. Electrolyses confirmed the process and gave faradic yield of 62% in cyanoacetic acid at potentials that are about 0.3 V less cathodic than the one required for Ni(salen).

## 1. Introduction

Electrocarboxylation of organic halides has been extensively studied as a synthetic method towards carboxylic acid [1–5]. Catalytic systems based on transition-metal complexes have proved to be an efficient way. Several nickel [6–8], palladium [9] and cobalt [10–12] complexes have been reported. Many works were devoted more specially on the electrosynthesis of cyanoacetic acid [13–16] whose derivatives are precious starting materials in pharmaceutical [17] and agrochemical [18] synthesis. Actually, the industrial manufacture of cyanoacetic acid is based on the reaction between chloroacetic acid and alkali metal cyanides [19]. This process is dangerous and environmentally unfriendly. For these reasons, the development of new synthetic ways has been appraised. Recently, Gennaro et al. have shown the electrocatalytic properties of a silver electrode for the synthesis of cyanoacetic acid through the reduction of chloroacetonitrile under  $\text{CO}_2$ .



The reduction of chloroacetonitrile occurs at a less cathodic potential (around 0.7 V) than those required on glassy carbon and the faradic yield (around 90%) is excellent [20]. Among the electrocatalysts based on transition-metal complexes, the best results were obtained with Ni(salen). Under an applied potential around  $-1.7$  V which represents a

high overpotential, a yield of 71% was reported [21]. Electrogenerated cobalt(I) complexes have also been used as catalytic systems for electrocarboxylation of organic halides [10,12]. The reported cobalt complexes present a square planar structure allowing the oxidative addition of alkyl halides on cobalt which seems to be the key step in the carboxylation process. Hexacoordinated cobalt complexes such as  $[\text{Co}(\text{phen})_3]^{2+}$  have never been used as potential catalysts due to the hexacoordination of Co(I) which would prevent the oxidative addition of alkyl halides [22,23]. However, it has been shown that the phenanthroline ligands are labile in the  $[\text{Co}(\text{II})(\text{phen})_3]^{2+}$  complex [24,25].

Here, we report for the first time, the electrocatalytic properties of  $[\text{Co}(\text{I})(\text{phen})_3]^+$  for the electrocarboxylation of chloroacetonitrile. Cyclic voltammetry studies reveal the activity of  $[\text{Co}(\text{I})(\text{phen})_3]^+$  towards chloroacetonitrile and  $\text{CO}_2$ . Preparative electrolyses were performed in order to calculate to the faradic yield of cyanoacetic acid.

## 2. Experimental

### 2.1. Reagents and equipments

1,10-phenanthroline, cobalt(II) chloride hexahydrated, chloroacetonitrile, and potassium hexafluorophosphate ( $\text{KPF}_6$ ) were used as received. Tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) was recrystallised from ethylacetate and dried at  $80^\circ\text{C}$  under vacuum. Acetonitrile (HPLC grade) was stored on molecular sieves (3 Å). Cyanoacetic acid was 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  $5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ . The  $[\text{Co}(\text{phen})_3](\text{PF}_6)_2$  was synthesized as described in the literature [24].

\* Corresponding author. Université de Toulouse, Université Paul Sabatier, Laboratoire de Génie Chimique, Bat. 2R1, 118 route de Narbonne, F-31062 Toulouse cedex 09, France. Tel.: +33 5 61 55 61 21; fax: +33 5 61 55 61 39.

E-mail address: reynes@chimie.ups-tlse.fr (O. Reynes).

## 2.2. Cyclic voltammetry and electrolyses

The cyclic voltammetry experiments were conducted in a classical three electrode cell under argon or carbon dioxide atmospheres. A saturated calomel electrode (SCE), a platinum wire and a glassy carbon (GC) disk (diameter: 3 mm) were used as reference, counter and working electrodes respectively. All experiments were carried out in dry acetonitrile + TBAPF<sub>6</sub> 0.1 mol L<sup>-1</sup>. Simulated voltammograms (ESP) have been computed with Nervi's program in order to evaluate the kinetic parameters [26].

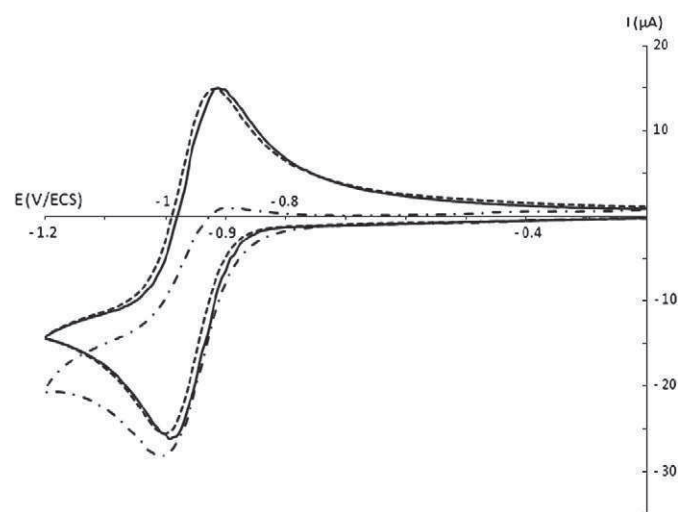
The electrolyses were performed in an undivided cell equipped with a magnesium bar used as a sacrificial anode, a saturated calomel electrode (SCE) as the reference electrode and carbon fibres as the working electrode. Acetonitrile + TBAPF<sub>6</sub> 0.1 mol L<sup>-1</sup> solution (volume 25 mL) containing chloroacetonitrile and [Co(II)(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> was saturated with carbon dioxide by bubbling during 30 min ([CO<sub>2</sub>] = 0.28 mol L<sup>-1</sup> [27]). The electrolysis potential was -1.4 V/SCE. The electrolyses were stopped when the current dropped to 10% of its initial value. The cyanoacetic acid was extracted using the procedure previously reported by Gennaro et al. [21].

## 3. Results and discussion

In the cathodic domain, the cyclic voltammograms of [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> in non-aqueous solvent under argon atmosphere exhibit three electrochemical reductions at -0.95 V, -1.65 V and -2.12 V corresponding to the Co(II)/Co(I), Co(I)/Co(-I) and free phenanthroline reductions respectively [22]. In a CO<sub>2</sub>-saturated solution, the catalytic reduction of CO<sub>2</sub> was demonstrated through the Co(I)/Co(-I) couple but it requires high overpotential [23].

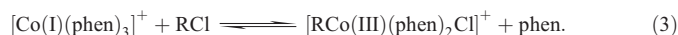
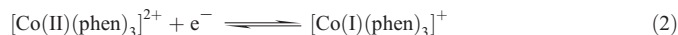
On the contrary, the Co(II)/Co(I) couple presents a nice reduction potential, around -1 V, but the unreactivity of Co(I) was attributed to the weak nucleophilicity of Co(I) and to a complete coordination sphere around the metal (three phenanthroline ligands) [22,23]. Nevertheless, the reactivity of Co(I) can be demonstrated.

Fig. 1 shows cyclic voltammograms of [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> in acetonitrile. As already described, curve A, the reduction of [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> into [Co(I)(phen)<sub>3</sub>]<sup>+</sup> follows a reversible monoelectronic process ( $E^\circ = 0.96$  V,  $k^\circ = 0.045$  cm s<sup>-1</sup>, evaluated by the  $\Delta E_p$  method [28] and simulated [26]). As expected, in a CO<sub>2</sub>-saturated solution, the voltammogram (curve B) is unchanged. No specific reaction between [Co(I)(phen)<sub>3</sub>]<sup>+</sup> and CO<sub>2</sub> takes place. On the contrary, under an argon atmosphere and after addition of chloroacetonitrile, the voltammo-



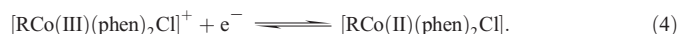
**Fig. 1.** Cyclic voltammograms in CH<sub>3</sub>CN + TBAPF<sub>6</sub>,  $v = 50$  mV/s. (—) 2 mmol L<sup>-1</sup> [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> under argon, (---) 2 mmol L<sup>-1</sup> [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> under carbon dioxide, and (-·-·-) 2 mmol L<sup>-1</sup> [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> and 8 mmol L<sup>-1</sup> chloroacetonitrile under argon.

gram (curve C) is severely modified. The electrochemical system appears irreversible and the cathodic peak is slightly increased. The reverse peak height increases when the potential scan speed is increased and decreases when chloroacetonitrile is added. This is typically an EC system in which the following reaction would be the oxidative addition of chloroacetonitrile (RCI) on the metal. This reaction implies the release of a phenanthroline ligand which has been observed for [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> [24,25]:

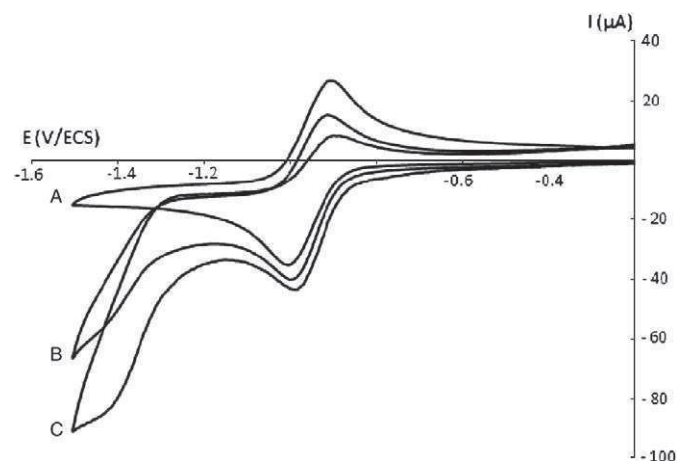
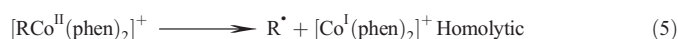


Assuming a simple EC scheme [30], the oxidative addition was evaluated through the RI<sub>p</sub> analysis ( $k$  around 60 M<sup>-1</sup>s<sup>-1</sup> [29] and simulated [26]). The kinetic constant ( $k$ ) is around 4 order of magnitude lower than those reported for planar Co(I)salen in the presence of *n*-butyl halides [30]. This suggests that the formation of the 16 electron complex, [Co(I)(phen)<sub>2</sub>]<sup>+</sup>, is the kinetic control step in the oxidative addition pathway. When free phenanthroline is added, the backward peak is increased which is in favour of the [Co(I)(phen)<sub>2</sub>]<sup>+</sup> formation assumption.

Fig. 2 shows cyclic voltammograms of [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> in acetonitrile under an argon atmosphere when the potential scan is reversed at -1.5 V before the reduction of Co(I) into Co(-I). Curve A is related to the reduction of [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> alone and curves B and C are the voltammograms when increasing amounts of chloroacetonitrile are added to the solution. As above mentioned, the signal of the Co(II)/Co(I) couple traduces the EC scheme ((2) and (3)). Moreover, a new cathodic peak appears at  $E_{pc} = -1.4$  V. The peak current increases with the chloroacetonitrile concentration but is not linearly related to the square root of the potential scan speed. A backward peak appears when the potential scan speed is higher than 9 V/s. The associated electrochemical system is the monoelectronic reduction [10] of the product of the oxidative oxidation (3), according to an ECE scheme (2, 3, 4):

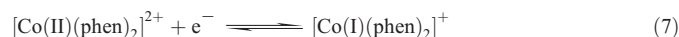


The resulting Co(II)-alkyl complex is known to undergo a rapid homolytic or heterolytic Co-R bond cleavage [10].



**Fig. 2.** Cyclic voltammograms in CH<sub>3</sub>CN + TBAPF<sub>6</sub> under argon,  $v = 100$  mV/s. (A) 2 mmol L<sup>-1</sup> [Co(II)(phen)<sub>3</sub>]<sup>2+</sup>, (B) 2 mmol L<sup>-1</sup> [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> and 4 mmol L<sup>-1</sup> chloroacetonitrile, and (C) 2 mmol L<sup>-1</sup> [Co(II)(phen)<sub>3</sub>]<sup>2+</sup> and 8 mmol L<sup>-1</sup> chloroacetonitrile.

Whatever is the cleavage, the global electron exchange is bielectronic: reduction (4) and reduction of the radical R' or reduction of  $\text{Co}^{\text{II}}(\text{phen})_2^{2+}$ . Indeed, the R'/R<sup>-</sup> potential is around  $-0.7\text{ V}$  [20] and according to the complexation coefficient  $\alpha$ , the E°(7) must be higher than E°(2).



The resulting  $\text{Co}^{\text{I}}(\text{phen})_2^+$  reacts with chloroacetonitrile through an oxidative addition; the kinetic constant  $k(8)$  must be higher than  $k(3)$  because of the under-coordination of  $\text{Co}^{\text{I}}(\text{phen})_2^+$ :



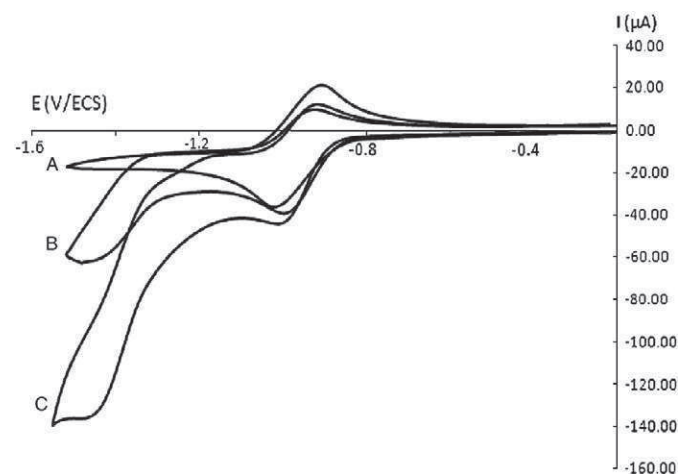
The catalytic cycle (4, 5/6, 7, 8) explains the catalytic peak current at  $E_{\text{pc}} = -1.4\text{ V}$  which increases with the chloroacetonitrile concentration. Note that the resulting carbanion can react with electrophilic compounds, acetonitrile or itself to form different compounds [31].

Fig. 3 gives the evidence of the  $\text{CO}_2$  activation by the  $[\text{RCo}(\text{II})(\text{phen})_2\text{Cl}]$  complex. As shown in Fig. 1,  $[\text{Co}(\text{I})(\text{phen})_3]^+$  does not react with  $\text{CO}_2$ . When  $[\text{Co}(\text{II})(\text{phen})_3]^{2+}$  and chloroacetonitrile are present in a  $\text{CO}_2$ -saturated solution (curve C), the intensity of the cathodic peak at  $E_{\text{pc}} = -1.4\text{ V}$  corresponding to the reduction (4) is greatly enhanced according to a catalytic process. The increase of the reduction current of  $[\text{RCo}(\text{III})(\text{phen})_2\text{Cl}]^+$  implies that  $\text{CO}_2$  enters in the catalytic cycle (4, 5/6, 7, 8) and interferes in the reduction of chloroacetonitrile. The mechanism could go through the addition of  $\text{CO}_2$  followed by the coupling of  $\text{CO}_2$  and the R substrate as reported for Ni or Pd complexes [6,9].



$[\text{Co}(\text{I})(\text{phen})_3]^+$  would be a catalyst for the electrocarboxylation of chloroacetonitrile according to a possible cycle (4, 9, 10, 11, 7, 8).

In order to confirm the formation of cyanoacetic acid, electrolyses were carried out in an undivided cell. In a  $\text{CO}_2$ -saturated acetonitrile solution (containing  $10^{-3}\text{ mol L}^{-1}$  of  $[\text{Co}(\text{II})(\text{phen})_3](\text{PF}_6)_2$  and a ten-



**Fig. 3.** Cyclic voltammograms in  $\text{CH}_3\text{CN} + \text{TBAPF}_6$ ,  $v = 100\text{ mV/s}$ . (A)  $2\text{ mmol L}^{-1}$   $[\text{Co}(\text{II})(\text{phen})_3]^{2+}$  under argon, (B)  $2\text{ mmol L}^{-1}$   $[\text{Co}(\text{II})(\text{phen})_3]^{2+}$  and  $4\text{ mmol L}^{-1}$  chloroacetonitrile under argon, and (C)  $2\text{ mmol L}^{-1}$   $[\text{Co}(\text{II})(\text{phen})_3]^{2+}$  and  $4\text{ mmol L}^{-1}$  chloroacetonitrile in a  $\text{CO}_2$ -saturated solution.

fold excess of chloroacetonitrile  $10^{-2}\text{ mol L}^{-1}$ ), the electrolyses were performed under potentiostatic conditions,  $E_{\text{applied}} = -1.4\text{ V}$ . The faradic yield calculated in cyanoacetic acid was  $62 \pm 1\%$  (the electric charge  $Q_{\text{passed}}$  was around  $47\text{ C}$  for a theoretic one  $Q_{\text{theoretic}}$  of  $52\text{ C}$ ) [32]. This good faradic yield was obtained at potentials that are about  $0.3\text{ V}$  less cathodic than one required for  $\text{Ni}(\text{salen})$  [21].

#### 4. Conclusion

We have shown that the  $\text{Co}(\text{I})$ phenanthroline complex is suitable for electrocarboxylation processes. The carboxylation follows the oxidative addition of chloroacetonitrile. No direct reduction of carbon dioxide was observed which enhances the selectivity of this electrocatalytic process. The preparative electrolyses show that cyanoacetic acid can be obtained with a good faradic yield under less cathodic working potentials compared to nickel(salen). Work is in progress for the development of the electrosynthesis procedure.

#### References

- [1] M.M. Baizer, J.L. Chruma, *J. Org. Chem.* 37 (1972) 1951.
- [2] O. Sock, M. Troupel, J. Perichon, *Tetrahedron Lett.* 26 (1985) 1509–1512.
- [3] A.A. Isse, A. Gennaro, *Chem. Commun.* (2002) 2798–2799.
- [4] G. Silvestri, S. Gambino, G. Filardo, A. Gulotta, *Angew. Chem. Int. Ed.* 23 (1984) 979–980.
- [5] O. Scialdone, A. Galia, G. Errante, A.A. Isse, A. Gennaro, G. Filardo, *Electrochim. Acta* 53 (2008) 2514–2528.
- [6] C. Amatore, A. Jutand, *J. Am. Chem. Soc.* 113 (1991) 2819–2825.
- [7] K. Osakada, R. Sato, T. Yamamoto, *Organometal* 13 (1994) 4645–4647.
- [8] A. Gennaro, A.A. Isse, F. Maran, *J. Electroanal. Chem.* 507 (2001) 124–134.
- [9] C. Amatore, A. Jutand, F. Khalil, M.F. Nielsen, *J. Am. Chem. Soc.* 114 (1992) 7076–7085.
- [10] A.A. Isse, A. Gennaro, E. Vianello, *J. Chem. Soc., Dalton Trans.* (1996) 1613–1618.
- [11] W.-H. Chung, P. Guo, K.-Y. Wong, C.-P. Lau, *J. Electroanal. Chem.* 486 (2000) 32–39.
- [12] G. Zheng, M. Stradiotto, L. Li, *J. Electroanal. Chem.* 453 (1998) 79–88.
- [13] D.A. Tyssee, *U.S. Pat.* 3, 945, 896 (1976).
- [14] B. Wermeckes, F. Beck, *Electrochim. Acta* 30 (1985) 1491–1500.
- [15] O. Scialdone, A. Galia, C. Belfiore, G. Filardo, G. Silvestri, *Ind. Eng. Chem. Res.* 43 (2004) 5006–5014.
- [16] O. Scialdone, M.A. Sabatino, A. Galia, G. Filardo, G. Silvestri, *J. Electroanal. Chem.* 614 (2008) 175–178.
- [17] P.M. Kinsey, *EP* 355986, (1990).
- [18] S.H. Davidson, *E.I. du Pont de Nemours and Co. US Pat.* 3,954, 992 (1973).
- [19] P. Pollak, A.G. Lonza, *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed. Wiley-VCH, Weinheim, 1998.
- [20] O. Scialdone, A. Galia, G. Filardo, A.A. Isse, A. Gennaro, *Electrochim. Acta* 54 (2008) 634–642.
- [21] A.A. Isse, A. Gennaro, *J. Electrochem. Soc.* 149 (2002) D113–D117.
- [22] G. Arena, R.P. Bonomo, S. Musumeci, E. Rizzarelli, *Z. Anorg. Allg. Chem.* 412 (1975) 161–169.
- [23] T.C. Simpson, R.R. Durand, *Electrochim. Acta* 33 (1988) 581–583.
- [24] B. Brisig, E.C. Constable, C.E. Housecroft, *New J. Chem.* 31 (2007) 1437–1447.
- [25] M. Matsumoto, J.H. Espenson, *J. Am. Chem. Soc.* 127 (2005) 11447–11453.
- [26] Copyright by Professor Carlo Nervi, this package can be downloaded at the Internet address: <http://www.lem.ch.unito.it/chemistry/electrochemistry.html>.
- [27] A. Gennaro, A.A. Isse, E. Vianello, *J. Electroanal. Chem.* 289 (1990) 203–215.
- [28] R.S. Nicholson, I. Shain, *Anal. Chem.* 37 (1965) 1351–1355.
- [29] R.S. Nicholson, I. Shain, *Anal. Chem.* 36 (1964) 706–723.
- [30] D. Pletcher, H. Thompson, *J. Electroanal. Chem.* 464 (1999) 168–175.
- [31] R. Barhadi, J. Gal, M. Heinz, M. Troupel, J. Périchon, *Tetrahedron* 49 (1993) 5091–5098.
- [32] Calculated as  $(Q_{\text{RCOOH}}/Q_{\text{passed}})$ . Where  $Q_{\text{RCOOH}} = 2 F N_{\text{RCOOH}}$  ( $N_{\text{RCOOH}}$  is the number of moles of cyanoacetic produced by electrolysis) and  $Q_{\text{consumed}}$  is the measured electric charge.