

Voltammetric analysis of the catalytic reactivity of electrogenerated Co^{I} –salen with organohalogenated derivatives in an ionic liquid at room temperature

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Abstract

We report in this study on the voltammetric investigation of the reactivity of a cobalt Schiff base complex, namely *N,N'*-bis(salicylidene)-ethylene diamino cobalt(II) so-called Co^{II} –salen in 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIm][PF₆], towards selected organohalogenated derivatives. The obtained results indicate that the electrochemical behavior of Co^{II} –salen in the room temperature ionic liquid is similar to that previously reported in various organic solvents. Also, the nature of the involved mechanisms of the electroreductive activation of the organohalogenated derivatives is almost unchanged in [BMIm][PF₆] compared with the usual conventional organic solvents.
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1. Introduction

Over the past few years, room temperature ionic liquids RTILs have re-attracted a wide range of sections of chemistry and generated much excitement and interest for various applications [1]. This renewed vigour is principally linked to the fact that these liquids have simple physical properties designing them as “green friendly solvents” (easy to recycle, non-volatile and non-flammable). Thus, they offer potential alternatives for a large variety of disciplines, especially organic and inorganic chemistries, and the use of RTILs in transition metal catalysis has been extensively developed. Striking works in this field have been recently reviewed [2,3]. Also, the development of RTILs for electrochemical applications is very attractive [4,5]. Several examples are now reported in the literature and most of them are related to the re-investigations of the electrochemical reactivity of selected organic and organometallic compounds in RTILs to offer an alternative to volatile organic solvents [6–12].

The most interesting reported results are that the nature of the investigated mechanisms is almost unchanged in RTILs compared with the usual conventional organic solvents [6,7,10,12].

We report in this study on the voltammetric investigation of the reactivity of a cobalt Schiff base complex, namely *N,N'*-bis(salicylidene)-ethylene diamino cobalt(II) so-called Co^{II} –salen in 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIm][PF₆] (see structures in Fig. 1), towards selected organohalogenated derivatives. This study provides a preliminary insight into the electroassisted catalytic intervention of the electrogenerated Co^{I} –salen intermediate in the reductive activation of trichloroacetic acid TCA, dichloroacetic acid DCA, dibromoethane DBE and benzyl chloride.

2. Experimental

Trichloroacetic acid, TCA, dichloroacetic acid DCA, dibromoethane DBE and benzyl chloride were reagent grade and used without purification (Aldrich). Co^{II} –salen

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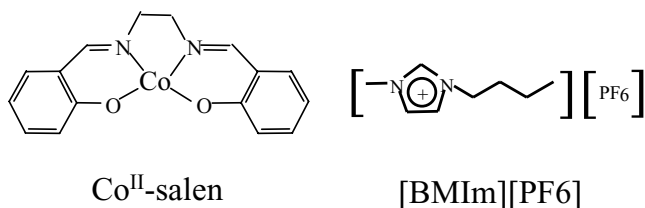


Fig. 1. structures of $\text{Co}^{\text{II}}\text{-salen}$ and $[\text{BMIm}][\text{PF}_6]$.

was purchased from Aldrich. Electrochemical experiments were carried out in $[\text{BMIm}][\text{PF}_6]$, conveniently prepared [13], with a conventional three-electrodes cell and a PC-controlled potentiostat/galvanostat (Tacussel). The working electrode was a vitreous carbon disk electrode from Radiometer-Tacussel exposing a geometrical area of 0.071 cm^2 and mounted in Teflon[®]. Hydrodynamic voltammetry experiments were conducted by rotating the disk electrode (Controvit device from Radiometer-Tacussel, France). The electrode was polished before each experiment with 3 and $0.3 \mu\text{m}$ alumina pastes followed by extensive rinsing with ultra-pure water. Platinum wire was used as counter electrode and saturated calomel electrode (sce), placed in a separate compartment was used as reference electrode. The potentials are also reported versus ferrocene/ferricinium, Fc/Fc^+ , potential value experimentally measured in our operational conditions. All the experiments were performed at ambient temperature and the electrolytic solutions were routinely deoxygenated with argon.

3. Results and discussion

The electrochemical behavior of $\text{Co}^{\text{II}}\text{-salen}$ complex is now well known in various organic solvents [14–16]. Typical examples of rotating disk electrode voltammogram (hydrodynamic voltammogram) and cyclic voltammogram of this complex (2 mmol l^{-1}) in $[\text{BMIm}][\text{PF}_6]$ are shown in Fig. 2. The hydrodynamic voltammogram (Fig. 2A) presents a well-defined anodic and a well-defined cathodic wave, both of equal current intensity, that can be related, by reference to the electrochemical behavior of the complex in several organic solvents [14–16], to the well-known $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}\text{-salen}$ oxidation and $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}\text{-salen}$ reduction processes, respectively. The half-wave potentials $E_{1/2}$ of these processes are 0.95 V versus sce and -1.22 V versus sce, respectively. The cyclic voltammogram (Fig. 2B, curve a) presents two well-defined reversible couples of peaks that can be related to $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}\text{-salen}$ and $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}\text{-salen}$ centered one-electron redox processes at 0.95 V versus sce and -1.22 V versus sce, respectively. These data clearly show that the electrochemical behavior of $\text{Co}^{\text{II}}\text{-salen}$ in $[\text{BMIm}][\text{PF}_6]$ is quite similar to that known in several organic solvents with emphasis on the fact that the potential value for the $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ redox process is more positive than that found in dimethylsulfoxide, dimethylformamide or

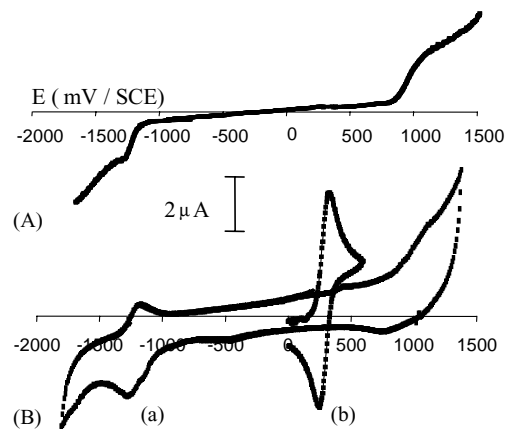


Fig. 2. (A) rotating disk electrode voltammogram (rotation rate = 800 rpm, potential scan rate = 5 mV/s) and (B) cyclic voltammograms (potential scan rate = 50 mV/s) of $\text{Co}^{\text{II}}\text{-salen}$ (2 mM , curve a) and ferrocene (curve b) in $[\text{BMIm}][\text{PF}_6]$ ionic liquid at a vitreous carbon electrode.

acetonitrile [14–16]. Also, it should be noted that the well observed reversibility of the $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ couple of peaks allows confirming the dryness of the used RTIL. Indeed, such a criterion was recently investigated by studying $\text{Ni}^{\text{II}}\text{-salen}$ complex in $[\text{BMIm}][\text{BF}_4]$ [7].

The cyclic voltammogram of ferrocene in $[\text{BMIm}][\text{PF}_6]$ is shown in Fig. 2B (curve b). It presents a well-defined reversible couple of peaks at 0.285 V versus sce. This result allows reporting the potential values of all the examined processes versus ferrocene/ferricinium Fc/Fc^+ standard couple in $[\text{BMIm}][\text{PF}_6]$ for a better comparison with previously reported values in various conditions. Table 1 recapitulates the obtained data.

Fig. 3 shows the cyclic voltammograms of $\text{Co}^{\text{II}}\text{-salen}$ (2 mmol l^{-1}) in $[\text{BMIm}][\text{PF}_6]$, restricted to the $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ centered one-electron redox process potential region, in the absence (curve a) and the presence of 5 mmol l^{-1} TCA, DCA and DBE (curves b, c and d, respectively). It clearly appears that upon addition of the organohalogenated derivatives, a large reduction current is developed at ca. -1.1 V versus sce while the corresponding re-oxidation peak of the $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ process disappeared. This means that the $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ redox couple of the complex is involved in the catalytic reduction of the organohalogenated derivatives, as it has been previously reported in several cases with similar complexes and in various solvents [17–22]. The expected catalytic process occurs via an outer sphere mechanism in which the electron transfer takes place between the active form of the catalyst $\text{Co}^{\text{I}}\text{-salen}$ and the substrate TCA, DCA or DBE. It should be noted that the direct reduction of these RX in $[\text{BMIm}][\text{PF}_6]$, occurs at ca. -1.91 , -1.82 and -1.83 V versus sce on carbon electrode (data not shown). Thus, these observations clearly show that the presence of the electrochemically generated $\text{Co}^{\text{I}}\text{-salen}$ drastically reduces the operational reduction potential of the examined organohalogenated derivatives by 0.8 V .

Table 1
Potential values of the studied redox processes in [BMIm][PF₆]

Redox process	$E_{1/2}$ (V) ^a	E_{pa} (V) ^b	E_{pc} (V) ^b
Ferrocene/ferrocinium	0.28 vs. sce	0.34 vs. sce	0.23 vs. sce
Co ^{III} /Co ^{II} -salen	0.95 vs. sce 0.66 vs. Fc/Fc ⁺	1.15 vs. sce 0.86 vs. Fc/Fc ⁺	0.74 vs. sce 0.46 vs. Fc/Fc ⁺
Co ^{II} /Co ^I -salen	-1.22 vs. sce -1.50 vs. Fc/Fc ⁺	-1.15 vs. sce -1.43 vs. Fc/Fc ⁺	-1.30 vs. sce -1.58 vs. Fc/Fc ⁺
TCA reduction			-1.10 vs. sce (with Co ^{II} -salen) -1.91 vs. sce (without Co ^{II} -salen)
DCA reduction			-1.10 vs. sce (with Co ^{II} -salen) -1.82 vs. sce (without Co ^{II} -salen)
DBE reduction			-1.10 vs. sce (with Co ^{II} -salen) -1.83 vs. sce (without Co ^{II} -salen)
Benzyl chloride reduction			-1.49 vs. sce (with Co ^{II} -salen) -2.05 vs. sce (without Co ^{II} -salen)

^a Hydrodynamic voltammetry measurement (rotation rate = 800 rpm; scan rate = 5 mV/s). $E_{1/2}$: half wave potential.

^b Cyclic voltammetry measurement (scan rate = 50 mV/s). E_{pa} : anodic peak potential; E_{pc} : cathodic peak potential.

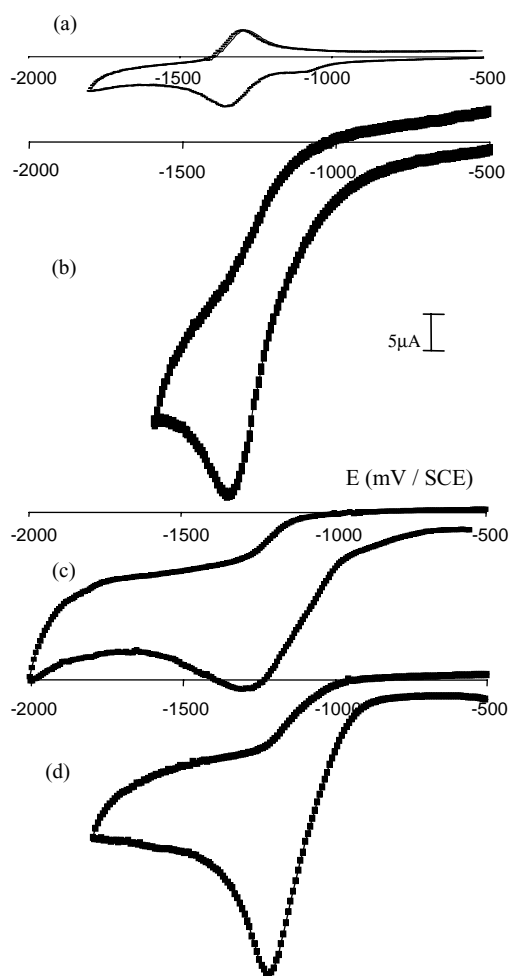


Fig. 3. Cyclic voltammograms (potential scan rate = 50 mV/s) of Co^{II}-salen (2 mM) in [BMIm][PF₆] ionic liquid at a vitreous carbon electrode, without (curve a) and with 5 mmol l⁻¹ of TCA (curve b), DCA (curve c) and DBE (curve d).

Upon addition of benzyl chloride (5 mmol l⁻¹) to Co^{II}-salen in [BMIm][PF₆], several changes in the cyclic voltammogram can be noticed (Fig. 4, curves a and b): (i) the reduction peak of Co^{II}/Co^I-salen process is slightly shifted (by 15 mV) toward more positive potential values, (ii) a new irreversible reduction peak appeared at approximately -1.49 V versus sce and (iii) Co^I/Co^{II}Salen reoxidation peak disappeared during the reverse anodic scan. This proves that the electrogenerated Co^I-salen fastly reacts with benzyl chloride (noted as RX), leading to the formation of the corresponding electroreducible R-Co^{III}-salen, as previously reported in the literature [14] in the general case

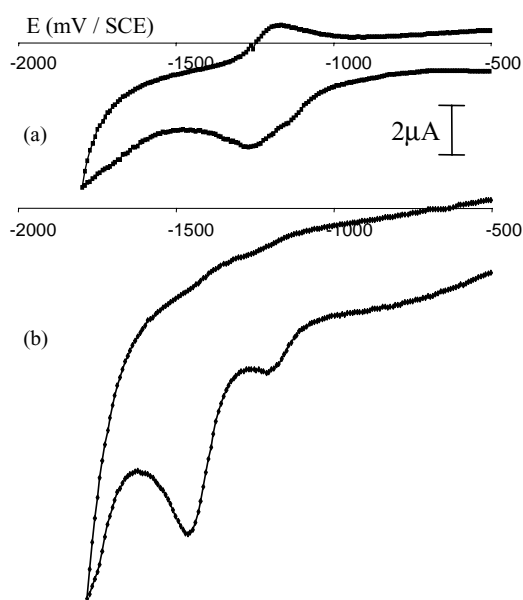


Fig. 4. Cyclic voltammograms (potential scan rate = 50 mV/s) of Co^{II}-salen (2 mM) in [BMIm][PF₆] ionic liquid at a vitreous carbon electrode, without (curve a) and with 5 mmol l⁻¹ of benzyl chloride (curve b).

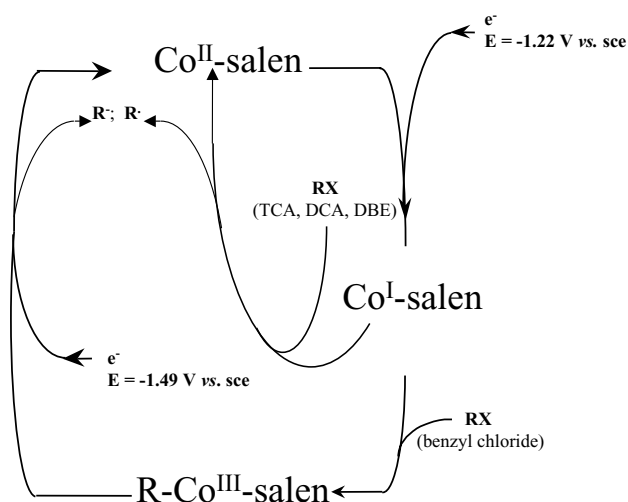


Fig. 5. Proposed electroassisted catalytic mechanisms of the examined organohalogenated derivatives (notes RX) in presence of Co^{II} -salen.

of organic solvents. Thus, these observations show that the electroassisted catalytic process occurs by an inner sphere mechanism in which benzyl-cobalt derivative is involved. Finally, it should be noted that the direct reduction of benzyl chloride in $[\text{BMIm}][\text{PF}_6]$ occurs at ca. -2.05 V versus sce on vitreous carbon electrode (data not shown). Thus, the presence of the electrochemically generated Co^{I} -salen drastically reduces the operational reduction potential of the organohalogenated derivatives by 0.5 V.

Fig. 5 recapitulates the possible electroassisted catalytic cycles for the reductive activation of TCA, DCA and DBE via an outer sphere mechanism and via an inner sphere mechanism for the activation of benzyl chloride.

4. Conclusion

Two remarkable observations can be emphasized from this preliminary study. First, the electrochemical behavior of Co^{II} -salen in the room temperature ionic liquid $[\text{BMIm}][\text{PF}_6]$ is similar to that previously reported in various organic solvents. Secondly, the nature of the in-

volved mechanisms of the electroreductive activation of organohalogenated derivatives is almost unchanged in RTILs compared with the usual conventional organic solvents. These observations, combined to that relative to the immobilization of the catalyst by using the ionic liquid allows us to confidently explore detailed studies to extend this investigation to the preparative scale, for the dehalogenation of selected derivatives.

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