

The Catalytic Feature of the $[\text{Co}(\text{bipy})_3]^{2+}/\text{CHCl}_3$ System in $\text{N,N}'$ -Dimethylformamide using Pulse Polarography

Denise Alves Fungaro and Roberto Tokoro*

Instituto de Química, USP, C.P. 20780, 01498-970 São Paulo - SP, Brazil

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Os estudos polarográficos de pulso envolvendo o sistema $[\text{Co}(\text{bipy})_3]^{2+}/\text{CHCl}_3$ em $\text{N,N}'$ -dimetilformamida mostraram comportamento polarográfico catalítico na ausência e presença de borohidreto de sódio. As constantes de velocidade das reações químicas paralelas encontradas são $4.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ na ausência de borohidreto e $4.43 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ na presença de borohidreto.

The pulse polarography studies on $[\text{Co}(\text{bipy})_3]^{2+}/\text{CHCl}_3$ in $\text{N,N}'$ -dimethylformamide solutions showed the polarographic catalytic behavior in the absence and presence of sodium borohydride. The rate constant of the parallel chemical reactions found is $4.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in the absence of borohydride and $4.43 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of borohydride.

Keywords: *electrocatalytic reduction, Co polypyridine complexes, chloroform*

Introduction

The redox electrochemistry of $[\text{Co}(\text{bipy})_3]^{2+}$ has been thoroughly investigated in the past¹⁻¹⁸. This complex yields a reduction wave corresponding to a reduction to a monovalent complex. The Cobalt(I) polypyridine complex is stabilized by the ligand field. Because the electrochemical behavior in aqueous or alcohol solutions is clearly not so simple, some other non-aqueous media were also used. It has been suggested¹⁹⁻²⁰ that electrogenerated $[\text{Co}(\text{bipy})_3]^+$ can function as a catalytic agent for the polarographic reduction of oxidizing-agent substrates. Vleck and Konrad²¹ observed cathodic catalytic currents of the tris(2,2'-bipyridine)Co(II) in the presence of carbon tetrachloride, chloroform and methylene chloride in ethanol-water mixtures using DC polarography. Margel and Anson²⁰ proposed a mechanism to explain the electrocatalytic reduction of allyl chloride by $[\text{Co}(\text{bipy})_3]^{2+}$ in acetonitrile. The same reaction was verified in an aqueous medium²².

The present paper reports the study of the catalytic cycle involving the electroreduction of $[\text{Co}(\text{bipy})_3]^{2+}$ in the presence of halogenated hydrocarbon in $\text{N,N}'$ -dimethylformamide (DMF) solutions using the dc and pulse polarography methods.

Experimental

Reagents

All chemicals were reagent grade and were used without further purification. Tris(2,2'-bipyridine)Co(II) per-

chlorate was prepared by the Burstall and Nyholm²³ method. Polarographic grade LiClO_4 was used as the supporting electrolyte. The DMF used was of spectrographic reagent grade.

Polarography

The polarograms were obtained with a Tacussel PRG5 and an EPL3 recorder using a cell with a three-electrode system. The dropping mercury electrode was the working electrode, and the drop time was 1.3 s. The reference electrode was a silver wire immersed in 0.04 M tetrabutylammonium iodide (TBAI) in a DMF solution which was doubly isolated by fritted glass disks from the bulk of the solution. A platinum wire was used as an auxiliary electrode. All solutions were deoxygenated by bubbling argon gas. The temperatures of the solutions were maintained by means of a water thermostat at 25.0 ± 0.1 °C. The potential scan rates during the recording of the polarograms was 10 mV s^{-1} . The pulse width employed was 75 ms in the pulse mode.

Coulometry

Coulometry experiments at a controlled potential were carried out in a conventional cell (Metrohm 6.1418.220) using a mercury pool electrode (14 cm^2 of geometrical area). The transferred charge was measured by using a current integrator IG6-N (Tacussel). The potential was applied with the Tacussel PRG5 instrument. Reference and auxiliary electrodes were individually isolated from the test

solution by glass frits. During the experiments, solutions were bubbled with argon and stirred with a magnetic bar.

Results and Discussion

Polarography of $1.0 \times 10^{-3} \text{ M } [\text{Co}(\text{bipy})_3]^{2+}$ presents one cathodic wave at -1.29 V attributed to a process involving one electron¹⁴. The intermediate $[\text{Co}(\text{bipy})_3]^+$ complex dissociates in DMF solution with the formation of new intermediate complexes with a smaller number of coordinated ligands on the electrode surface¹³. Chloroform (CHCl_3) gives a two-electron reduction wave at -1.50 V , and an identical polarogram is obtained in the presence of free bipyridine. Figure 1 shows the normal pulse polarograms of $1.0 \times 10^{-3} \text{ M } [\text{Co}(\text{bipy})_3]^{2+}$ with the initial potential fixed at 0 V , obtained in different CHCl_3 concentrations. Upon the addition of chloroform to these solutions, the limiting currents of these waves increased in height.

The dependence of these wave heights on analytical chloroform concentration is shown in Fig. 2. The limiting current was measured at a suitable potential (-1.40 V) on the plateau of the waves and increases in accordance with a curve similar in form to the Langmuir adsorption isotherms. Similar curves are also obtained at a fixed CHCl_3 concentration by changing the $[\text{Co}(\text{bipy})_3]^{2+}$ concentration.

Exhaustive controlled-potential coulometry of the solution of $[\text{Co}(\text{bipy})_3]^{2+}$ with excess 2,2'-bipyridine results in the quantitative formation of the intensively blue $[\text{Co}(\text{bipy})_3]^+$ ion. The addition of chloroform after exhaustive coulometry on blue $[\text{Co}(\text{bipy})_3]^+$ causes the disappearance of the blue color giving way to the original yellow color of the solution. The normal pulse polarogram of this remaining solution shows a catalytic wave profile similar to that obtained in Fig. 1.

These results suggest the existence of a catalytic cycle where the electrogenerated $[\text{Co}(\text{bipy})_3]^+$ reacts with CHCl_3 forming an intermediate unstable mixed complex. This reaction results in the regeneration of cobalt(II) at the electrode surface, and this accounts for the enhancement in the limiting current of the cobalt(II) bipyridine complex.

The mechanisms of the catalytic electrode reactions of $[\text{Co}(\text{bipy})_3]^{2+}$ taking place in the presence of chloroform may be indicated as follows:

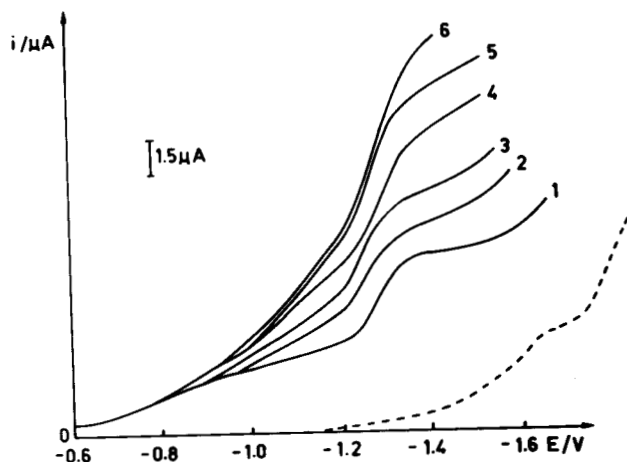
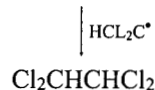
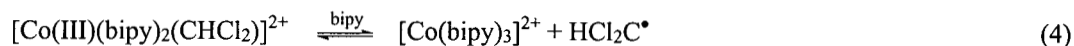
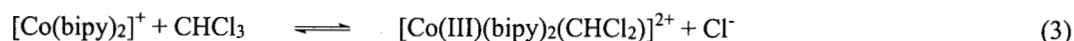
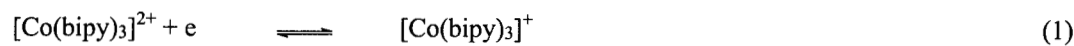


Figure 1. Normal pulse polarograms of $1.0 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+} + 0.1 \text{ M LiClO}_4/\text{DMF}$ at different CHCl_3 concentrations: 1) 0 , 2) $2.0 \times 10^{-4} \text{ M}$, 3) $4.0 \times 10^{-4} \text{ M}$, 4) $8.0 \times 10^{-4} \text{ M}$, 5) $1 \times 10^{-3} \text{ M}$; and 6) $1.6 \times 10^{-3} \text{ M}$. Initial potential: 0 V . ($5 \text{ mM CHCl}_3 + 0.1 \text{ M LiClO}_4/\text{DMF}$ in dashed line).

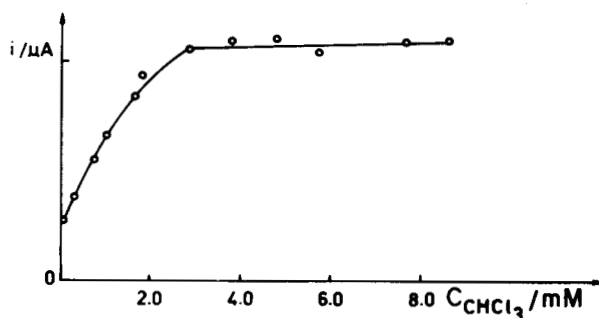


Figure 2. Dependence of the limiting current with the concentration of CHCl_3 for $1.0 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+} + 0.1 \text{ M LiClO}_4/\text{DMF}$.

The results described support the general features of the scheme proposed by Margel and Anson²⁰ to explain the catalytic reduction of allyl halides by tris(2,2'-bipyridine)Co(II) in acetonitrile. Kamau and Rusling²² agree with the Margel and Anson proposal studying the reduction of allyl chloride by tris(2,2'-bipyridine)Co(II) in aqueous micellar solutions. Evidence for the organocobalt complex intermediate has been thoroughly described in the literature, and these compounds play a very important role in homogeneous catalysis^{24,25}

The release of the chloride anion in the decomposition of the mixed complex was confirmed by the appearance of the oxidation wave for mercury in the presence of chloride at +0.35 V using reverse pulse polarography (RPP). The reverse pulse polarograms of the CHCl₃ solution (Fig. 3a) and the solution containing only [Co(bipy)₃]²⁺ (Fig. 3b) with initial potential at -1.1 V, show no wave for free chloride. This anodic wave appears only for the [Co(bipy)₃]²⁺ + CHCl₃ solution (Fig. 3c). This experiment was also repeated with an initial potential at -0.70 V, and no anodic wave at +0.35 V was observed. It can be concluded that the anodic wave at +0.35 V appears only under conditions where [Co(bipy)₂]⁺ is generated at the electrode surface and reacts with the CHCl₃ present in the solution, because at -1.1 V the chloroform is not reduced directly.

The values of the ratio of the mean limiting current (\bar{i}_l) to mean diffusion current (\bar{i}_d) are obtained from dc polarograms and applied to the calculation of the apparent chemical rate constant using Koutecky equations^{26,27}. This method gives the value of the rate constant as $4.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Vlcek and Konrad²¹ determined the overall rate constant being of the order $2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ for [Co(bipy)₃]Cl₂ + CHCl₃ in ethanol-water mixtures. In protic media, the electrophilic species is competitive with the halogenated hydrocarbon by the intermediate cobalt(I) complex.

The polarographic catalytic process of the [Co(bipy)₃]²⁺/CHCl₃ system in DMF in the presence of NaBH₄

The chemical reduction of CHCl₃ with sodium borohydride non-aqueous media is very slow. When the Tris(2,2'-bipyridine)Co(II) complex is present, even in small traces, CHCl₃ reacts with sodium borohydride very rapidly, even violently, at higher concentrations of the reagents. The reaction involves the Co(I) bipyridyl complex, and stable organometallic derivatives can be obtained^{24,28,29}. The electrochemical behavior of these solutions was investigated to illuminate on the mechanism of the process.

The polarographic reduction of 5.0 mM CHCl₃ + 1.0 mM NaBH₄ presents one cathodic wave at -1.50 V (Fig. 4a), which is identical to that in the absence of borohydride

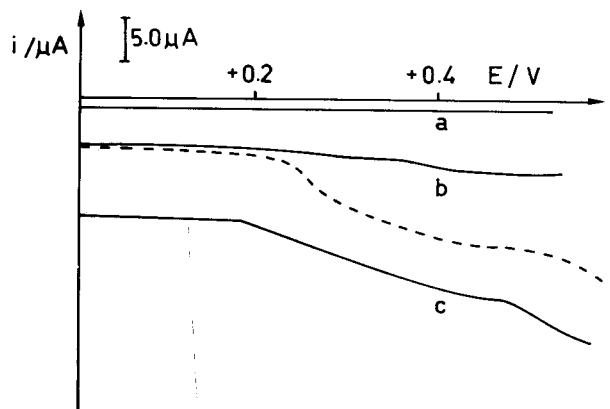
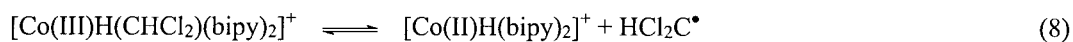
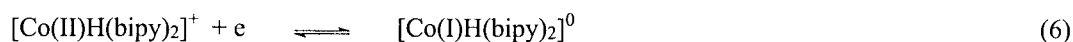
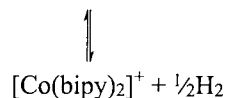
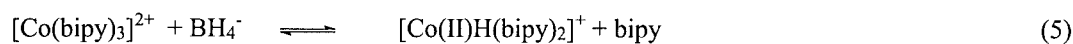


Figure 3. Reverse pulse polarograms of 0.1 M LiClO₄/DMF and: a) 5.0 mM CHCl₃, b) 1.0 mM [Co(bipy)₃]²⁺; and c) (a) + (b). (5 mM LiCl in dashed line). Initial potential: -1.1 V.

when the polarograms are compared at the same current scale. The polarogram of 1.0 mM [Co(bipy)₃]²⁺ + 1.0 mM NaBH₄ solution shows one-electron wave at -1.19 V (Fig. 4b). The anodic wave at +0.25 V for the oxidation of borohydride was not observed, indicating the consumption of borohydride because of its reaction with the Co(II) bipyridine complex forming hydride-intermediates^{28,29}. When CHCl₃ was added to the solution of 1.0 mM [Co(bipy)₃]²⁺ + 1.0 mM NaBH₄ (Fig. 4c), the limiting cathodic current of the Co(II) complex increased and catalytic behavior was observed.

The reaction mechanism of the catalytic wave can be represented formally by the scheme below.

The first step (Eq. 5) is the homogeneous redox reaction between the Co(II) complex and borohydride. The heterogeneous reaction (Eq. 6) is the reduction of the Co(II) hydride complex to the Co(I) hydride complex. The hydride complex reacts with chloroform via Eq. 7 to yield an unstable organocobalt intermediate. The regeneration of [Co(bipy)₂]⁺ in the sequence of Reaction 8, which re-enters the catalytic cycle via Eq. 6 accounts for the enhancement of the reduction wave. The intermediate hydride complex, tetrachloroethane, and the organometallic species have been reported in the literature^{224,28,29}.



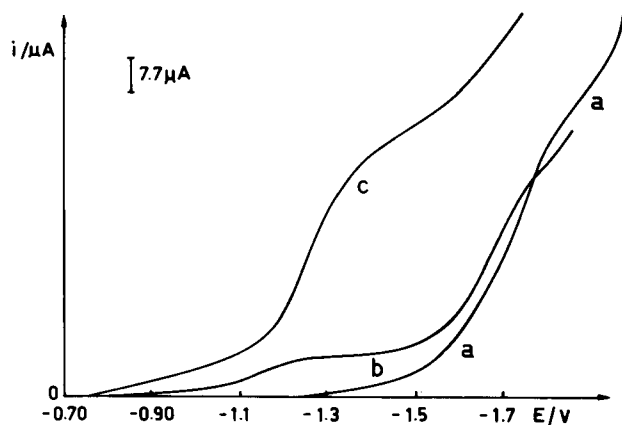


Figure 4. Normal pulse polarograms of 0.1 M LiClO₄/DMF and: a) 5.0 mM CHCl₃ + 1.0 mM NaBH₄, b) 1 mM [Co(bipy)₃]²⁺ + 1.0 mM NaBH₄; and c) (a) + (b). Initial potential: 0 V.

Figure 5 presents the plot of the catalytic current against the NaBH₄ concentration in 1.0 mM [Co(bipy)₃]²⁺ + 1.0 mM CHCl₃ solution. The limiting current was measured at -1.40 V using normal pulse polarography. In the absence of borohydride, chloroform reacts with the [Co(bipy)₂]⁺ complex generated on the electrode surface via Eqs. 1-4. With the addition of borohydride, the catalytic current increases until 1.0 mM NaBH₄. The height of the wave decreases beyond 1.0 mM NaBH₄. Simultaneously, the color of the initial yellow solution changed. It develops a deep blue color with 4.8 mM NaBH₄ and a green color at a concentration > 20 mM NaBH₄.

The results that have been observed after the addition of NaBH₄ to the [Co(bipy)₃]²⁺/CHCl₃ system can be accommodated on the basis in the suggested Eqs. 5-8. Initially the rate-determining step is Eq. 5. The catalytic current increases linearly as the concentration of added borohydride is increased. When NaBH₄ is in excess in relation to the concentration of [Co(bipy)₃]²⁺, Eq. 7 becomes slower. The persistence of the blue color in the solution confirms this. Simultaneously, the magnitude of the wave is suppressed as a result of the gradual stabilization of the intermediate organometallic complex via Eq. 7. With more concentrated borohydride solutions (> 20 mM) the cathodic wave at -1.24 V disappears and the solution develops a green color due to the formation of a stable organometallic intermediate. The change of the initial deep blue solution to green is also obtained at a fixed [Co(bipy)₃]²⁺ (1.0 mM) and borohydride (100 mM) concentration by changing the CHCl₃ concentration.

The apparent chemical rate constant (k) was determined using the Koutecky equations^{26,27} and the experimental values of \bar{i}_l/\bar{i}_d were obtained by the curve-fitting method. We estimated a value for k of $4.43 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The rate constant of the [Co(bipy)₃]²⁺/CHCl₃ system in DMF is ca. tenfold greater in the presence of borohydride than in its absence. The results suggest the involvement of the cobalt-

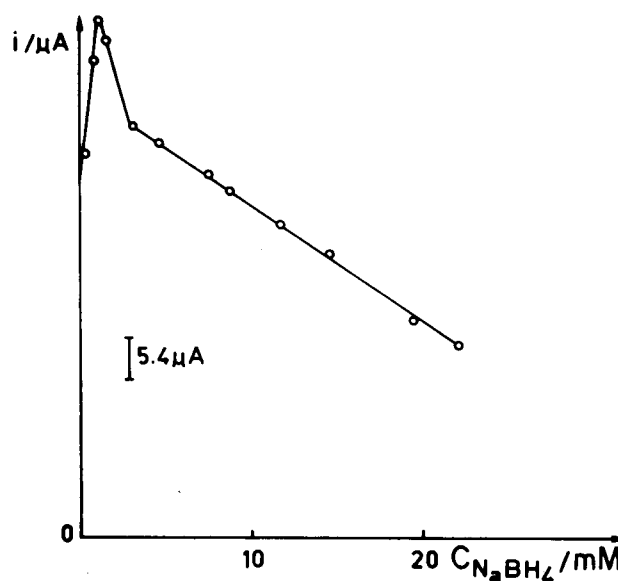


Figure 5. Dependence of the limiting current with the concentration of NaBH₄ for 1.0 mM [Co(bipy)₃]²⁺ + 1.0 mM CHCl₃ + 0.1 M LiClO₄/DMF.

hydride complex intermediate in the NaBH₄ solution, because according to the literature in the case of oxidizing agents which react with hydride-ion transfer, the rates of homogeneous oxidation are ca. $10^4 \text{ M}^{-1} \text{ s}^{-1}$ ³⁰. Previous studies on selective hydrogenation of 1,3-diolefins by cobalt(I)-bipyridyl complexes also show that the role of NaBH₄ is as a reductant as well as a reagent for producing cobalt-hydride complexes³¹. A disadvantage in the borohydride solution is a gradual decrease of the catalytic activity when the formation of stable organometallic derivatives begins. Therefore, for quantitative polarographic determinations an excess of borohydride in the [Co(bipy)₃]²⁺/CHCl₃ system should be avoided.

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References

1. B. Martin and G.M. Waind, *Proc. Chem. Soc.* **169**, (1958).
2. A.A. Vlcek, *Nature*, **180**, 573 (1957).
3. E. Paglia and C. Sironi, *Gazz. Chim. Ital.* **87**, 125 (1957).
4. G.M. Waind and B. Martin, *J. Inorg. Nucl. Chem.* **8**, 551 (1958).
5. A.A. Vlcek, *Z. Physik. Chem. (sonderheft)* **143**, (1958).
6. P. Silvestroni and L. Ceciarelli, *Ric. Sci. Suppl.* **30**, 1760 (1960).
7. S. Cabani, *Gazz. Ital.* **90**, 1410 (1960).
8. B. Martin, W.R. McWhinnie and G.M. Waind, *J. Inorg. Nucl. Chem.* **23**, 207 (1961).

9. A.A. Vleck, *Prog. Inorg. Chem.* **5**, 211 (1963).
10. E.A. Osipova, G.V. Prokhorova, P.K. Agasyan and S.V. Rudometkin, *J. Anal. Chem. USSR* **38**, 530 (1983).
11. G.N. Kamau, T. Leipert, S.S. Shula and J.F. Rusling, *J. Electroanal. Chem.* **233**, 173 (1987).
12. J. Hanzlik, J. Hovorka and A.M. Camus, *Coll. Czech. Chem. Commun.* **52**, 838 (1987).
13. G.K. Budnikov, T.N. Kozitsyna and V.A. Mikhailov, *Zh. Obshch. Khim.* **41**, 2132 (1971).
14. S.K. Dhar and W.E. Kurcz, *J. Electroanal. Chem.* **53**, 325 (1974).
15. Y. Sato, *Bull. Chem. Soc. Jpn.* **47**, 2065 (1965).
16. T. Saji and S. Aoyagui, *J. Electroanal. Chem.* **60**, 1 (1975).
17. R. Prasad and D.B. Scaife, *J. Electroanal. Chem.* **87**, 373 (1977).
18. J.M. Rao, M.C. Hughes and D.J. Macero, *Inorg. Chim. Acta* **35**, L369 (1971).
19. S. Margel, W. Smith and F.C. Anson, *J. Electrochem. Soc.* **124**, 241 (1978).
20. S. Margel and F.C. Anson, *J. Electrochem. Soc.* **125**, 1232 (1978).
21. D. Konrad and A.A. Vleck, *Proc. Symp. Coord. Chem. Tihany Hung.* **265**, (1964).
22. G.N. Kamau and J.F. Rusling, *J. Electroanal. Chem.* **240**, 217 (1988).
23. F.H. Bustall and R.S. Nyholm, *J. Chem. Soc.* **3570**, (1952).
24. G. Mestroni, A. Camus and E. Mestroni, *J. Organometal. Chem.* **24**, 775 (1970).
25. L. Levitin, M. Dvolaitzky and M.E. Vol'Pin, *J. Organometal. Chem.* **C37** (1971).
26. J. Koutecky, *Coll. Czech. Chem. Commun.* **18**, 311 (1953).
27. J. Koutecky, *Chem. Listy* **47**, 9 (1953).
28. G. Mestroni, A. Camus and C. Cocevar, *J. Organometal. Chem.* **29**, C17 (1971).
29. A. Camus, C. Cocevar and G. Mestroni, *J. Organometal. Chem.* **39**, 355 (1972).
30. G.K. Budnikov, O.Yu. Kargina and I.F. Abdullin, *J. Anal. Chem. URSS* **44**, 1369 (1989).
31. H. Kanai, N. Yamamoto, K. Kishi, K. Mizuno and K. Tarama, *J. Catal.* **73**, 228 (1982).