

Article

Polarographic Studies of Cobalt (II)-Bipyridyl Complexes in the Presence of Sodium Borohydride in Water-Dimethylformamide Mixtures

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A redução do $[\text{Co}(\text{bipy})_3]^{2+}$ em soluções de água-dimetilformamida (2:1) foi realizada quimicamente por borohidreto de sódio. A solução azul-escuro obtida mostrou comportamento eletroquímico diferenciado com a variação da quantidade de borohidreto utilizada na redução. Foi proposto que hidretos complexos intermediários formam-se em solução. Os estudos polarográficos mostraram também uma onda anódica catalítica em $-1.10 \text{ V x E.C. NaCl } 3 \text{ M}$.

The reduction of $[\text{Co}(\text{bipy})_3]^{2+}$ in water-dimethylformamide (2:1) solutions was chemically performed with sodium borohydride. The deep blue solution obtained showed different electrochemical behavior with varying amounts of borohydride. Intermediate hydride-complexes which form in solution were proposed. The polarographic studies showed also an anodic catalytic wave at $-1.10 \text{ V x E.C. } 3 \text{ M NaCl}$.

Keywords: *hydride complexes, electrocatalytic wave, Co polypyridine complexes*

Introduction

The deep blue complex $[\text{Co}(\text{bipy})_3]^+$ ($\lambda_{\text{max}} = 600 \text{ nm}$) can be chemically prepared by reducing $[\text{Co}(\text{bipy})_3]^{2+}$ or $[\text{Co}(\text{bipy})_3]^{3+}$ in the presence of excess 2,2'-bipyridine with sodium borohydride. The compound of the Co (I) complex is relatively stable in the absence of oxygen and is slightly soluble in water¹.

The reduction of transition metal complexes of 2,2'-bipyridine with sodium borohydride is considered to proceed via labile hydride-intermediates, which may be trapped by the addition of ligands such as triphenylphosphine²⁻⁶. Transition-metal hydrides are important stoichiometric reagents and catalyze many reactions, including the water-gas shift reaction and hydrogenation, hydroformylation, hydrosilylation and polymerization of olefins⁷. Electrochemical methods, specially polarographic techniques, can provide information concerning the chemical reactions involving the intermediate hydride-complexes in a catalytic system.

This paper reports on a study of the electrochemical behavior of $[\text{Co}(\text{bipy})_3]^{2+}$ solutions in the presence of an

excess of sodium borohydride. The kinetics and mechanism of the homogeneous chemical reduction of $[\text{Co}(\text{bipy})_3]^{2+}$ with NaBH_4 was also considered.

Experimental

Reagents

All chemicals were reagent grade and were used without further purification. $[\text{Co}(\text{bipy})_3](\text{ClO}_4)_2$ (bipy = 2,2'-bipyridine) was prepared as previously described⁸. Polarographic grade 0.067 M tetraethylammonium bromide (TEAB) was used as the supporting electrolyte. The solvents were spectrophotometric grade N,N'-Dimethylformamide (DMF) and distilled water.

Polarography

The polarograms were obtained with a Tacussel PRG 5 and an EPL 3 recorder using a three-compartment electrochemical cell. The dropping mercury electrode was mechanically controlled and the drop time was 1.3 s. The calomel reference electrode (3 M NaCl) was isolated from the bulk solution by a glass frit. The auxiliary electrode was

a platinum wire. Solutions were deoxygenated with pure argon (99.999%). The temperature was 25 °C in all experiments. The potential scan rate was 10 mV.s⁻¹. Pulse widths employed were 75 ms in the pulse mode.

Results and Discussion

Preliminary experiments

On the addition of solid sodium borohydride to an aqueous [Co(bipy)₃]²⁺ solution, the BH₄⁻ immediately reacts with water, and a considerable amount of hydrogen is liberated. The complex reduction is a slower reaction than the borohydride reaction with water. The reducing ability of the borohydride solution is diminished due to this parallel reaction and a large excess of borohydride is required to carry out the total complex reduction.

The alkali-metal borohydride is stable in a highly basic medium⁹ and in aprotic solvents. However, the blue cobalt (I) complex is unstable in alkaline solution¹⁰. Thus, qualitative experiments were carried out with aprotic solvents (acetonitrile, dimethyl sulfoxide etc.), and DMF proved to be the most suitable. The physicochemical properties of DMF supports its use as a solvent in hydride chemistry¹¹. Sodium borohydride in DMF is stable for several days. When [Co(bipy)₃] (ClO₄) aqueous solution was treated with sodium borohydride in DMF, the reduction took place immediately, forming a stable deep blue solution.

Spectrophotometric studies on [Co(bipy)₃]²⁺/NaBH₄ solutions showed that a water - DMF medium with ca. 2:1 composition, with a maximum stability for the complex concentrations ranging from 0.10 to 1.0 mM can be obtained.

Polarography of [Co(bipy)₃]²⁺ in the presence of sodium borohydride

The polarograms of 1 × 10⁻³ M [Co(bipy)₃]²⁺ solution with different additions of NaBH₄ in DMF (0 to 0.25 M)

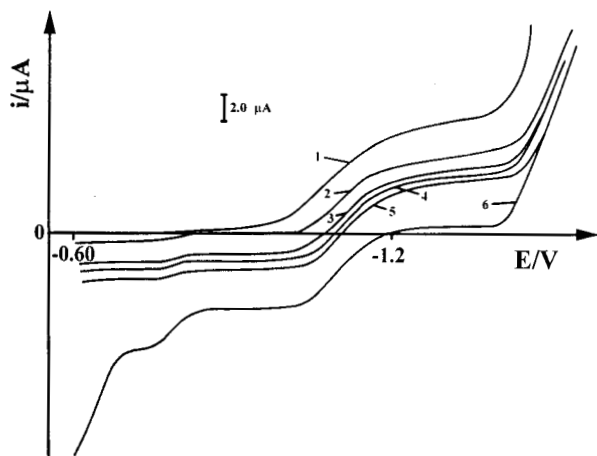
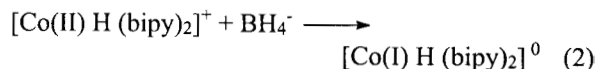
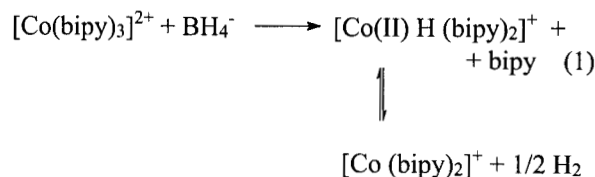


Figure 1. Tact polarograms of 1 mM [Co(bipy)₃]²⁺ at different NaBH₄ concentrations. 1) 0; 2) 4.1 mM; 3) 8.8 mM; 4) 12.3 mM; 5) 17.6 mM; 6) 250 mM.

are shown in Fig. 1. In the absence of borohydride the [Co(bipy)₃]²⁺ solution exhibited a cathodic wave at -1.07 V. The first reduction step and the first oxidation step for the Co(II)/bipy complex is a reversible one-electron step in aqueous^{1,10} or non-aqueous media¹². The original yellow solution changed to blue on the addition of 4.0 mM NaBH₄, and the half-wave potential of the cathodic wave shifted 30 mV toward a more negative potential. At more concentrated borohydride solutions the cathodic component decreased and the anodic component merged, affording a composite wave. Finally, an anodic wave was observed which showed catalytic behavior. A color change in the [Co(bipy)₃]²⁺ solution when NaBH₄ 4 mM was added was not observed.

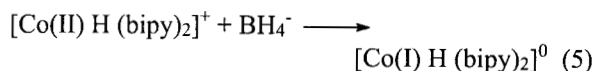
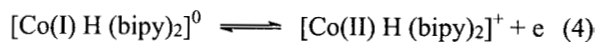
The experimental data showed that hydride-complexes are involved in the electrochemical process. The chemical reaction between [Co(bipy)₃]²⁺ and BH₄⁻ takes place with the formation of the hydride [Co(II)H(bipy)₂]⁺ (A) and subsequent [Co(I)H(bipy)₂]⁰ (B) in the bulk of the solution, according to the formal scheme:



Hydride-complex A is electrochemically reduced to hydride-complex B in the following reaction:



The cathodic and anodic waves can be described by this electrode process. A mixture of A and B in the solution gives a mixture of cathodic and anodic currents corresponding to the relative concentration of each species. The anodic wave shows catalytic behavior in the presence of a large excess of borohydride. The mechanism of the anodic catalytic currents can be outlined as follows:



The hydrogen ion in a transition-metal complex has a very large ligand-field strength, which is manifested by a shift in the E_{1/2} of the [Co(bipy)₃]^{2+/+} reduction to more negative potentials. The borohydride ions may function as a source of hydride ions and also as a reducing agent. Parallel reactions in the solution are involved such as substitution or dissociation of the initial complex with solvent molecules, reaction of BH₄⁻ with water,

reaction of the hydride-complex with water etc. The hydride-complexes were represented by formal oxidation states.

The hydride-complexes can be stabilized by ligands with high ligand-field strength (for example, tertiary phosphines or cyanide). These ligands are more useful for stabilizing hydride-complexes than conjugated chelating ligands, such as 2,2'-bipyridine. It has been shown that hydride-complexes with 2,2'-bipyridine are unstable in air and moisture, but can be isolated and characterized in the presence of tertiary phosphines^{2-4,13}. The preparation of the hydride-complex of cobalt (I) with phosphine ligands has been previously described^{14,15}.

Borohydride concentration

The dependence of the wave heights of the 1×10^{-4} M $[\text{Co}(\text{bipy})_3]^{2+}$ solution on borohydride concentration is shown in Fig. 2. The limiting current was measured at a suitable potential on the plateau of the waves. Progressive lowering of the cathodic current and the concomitant increase of the anodic current were observed with an increase in the borohydride concentration. Beyond 40 mM NaBH_4 , the wave became totally anodic and the current increased sharply.

Cobalt (II) bipyridine concentration

The height of the wave, measured at the limiting current, is shown in Fig. 3 as a function of the concentration of $[\text{Co}(\text{bipy})_3]^{2+}$ for 3.3×10^{-2} M NaBH_4 solutions. The cathodic current increased linearly, showing the tendency to remain unchanged at concentrations ≥ 3.0 mM of the Co(II) complex. Similarly, the anodic current increased linearly until it reached a steady state at ca. 1.0 mM $[\text{Co}(\text{bipy})_3]^{2+}$. Thus, experimental evidence indi-

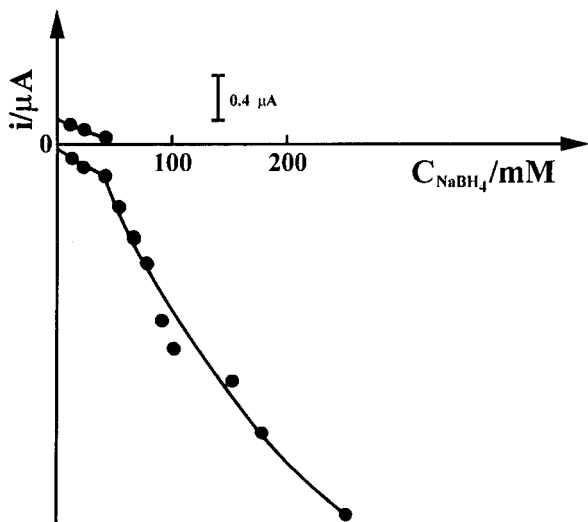


Figure 2. Dependence of the current on the concentration of NaBH_4 for 1×10^{-4} M $[\text{Co}(\text{bipy})_3]^{2+}$ + 0.067 M TEAB.

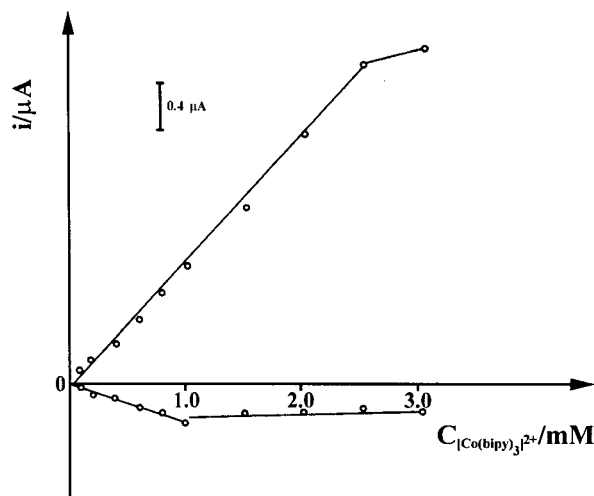


Figure 3. Dependence of the current on the concentration of $[\text{Co}(\text{bipy})_3]^{2+}$ for 3.3×10^{-2} M NaBH_4 + 0.067 M TEAB.

cates that Reaction 2 is slower than Reaction 1. This experiment was repeated with a 3.0×10^{-1} M NaBH_4 solution by changing the Co(II) complex concentration (Fig. 4). The solution presented an anodic wave which increased linearly. Beyond the 3.6×10^{-3} M Co(II) complex, the anodic current falls as a result of the precipitation of the dark-blue compound.

2,2'-bipyridine concentration

The composite wave of the 0.50×10^{-3} M $[\text{Co}(\text{bipy})_3]^{2+}$ + 0.05 M NaBH_4 solution at -1.10 V presented a decrease in the anodic current and an increase in the cathodic current as the concentration of the added bipy (2.0 mM to 10 mM) was increased. The anodic wave obtained from a 0.50×10^{-3} M $[\text{Co}(\text{bipy})_3]^{2+}$ + 0.10 M NaBH_4 solution decreased upon the addition of free bipyridine (2.0 mM to 10 mM). Similarly, the half-wave potential shifted to a more positive potential in both cases. This fact indicates that one molecule of bipyridine is lost when the Co(II) complex is reduced with NaBH_4 . The addition of bipyridine stabilizes the complex $[\text{Co}(\text{bipy})_3]^{2+}$ and the formation of the hydride-complex becomes unfavorable.

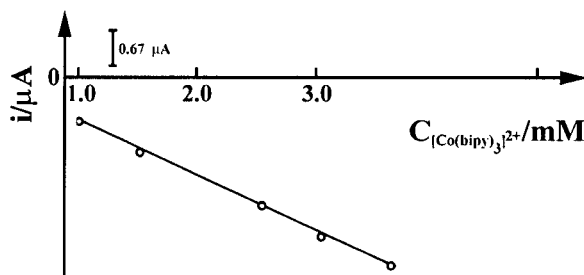


Figure 4. Dependence of the current on the concentration of $[\text{Co}(\text{bipy})_3]^{2+}$ for 3.3×10^{-1} M NaBH_4 + 0.067 M TEAB.

Kinetic reactions

The study of the kinetics of the homogeneous $[\text{Co}(\text{bipy})_3]^{2+}$ reduction with sodium borohydride was followed by recording time variations in the polarographic limiting currents of polarographically active species. The cathodic wave of the $1.0 \times 10^{-3} \text{ M } [\text{Co}(\text{bipy})_3]^{2+} + 4.0 \text{ mM NaBH}_4$ solution remained unchanged up to 2 h, however the blue solution became unstable at the end of this period. The polarogram of the $1.0 \times 10^{-3} \text{ M } [\text{Co}(\text{bipy})_3]^{2+} + 50 \text{ mM NaBH}_4$ solution presented a decrease of the cathodic component and an increase of the anodic component for 10 min. After this period, the waves were not affected for up to 2 h. The anodic wave of the $1.0 \times 10^{-3} \text{ M } [\text{Co}(\text{bipy})_3]^{2+} + 100 \text{ mM NaBH}_4$ solution exhibited a sharp decrease with increasing time up to 2 h. The respective cathodic current was not simultaneously observed. The electrochemical behavior of the $[\text{Co}(\text{bipy})_3]^{2+}/\text{NaBH}_4$ system with time indicates that the mechanism of the homogeneous reduction involves the slow formation of the hydride-complex of Co(I), and side reactions such as BH_4^- with water and hydride-complexes with water.

Polarographic reduction of $[\text{Co}(\text{bipy})]^{2+}$ presents one cathodic wave at -1.29 V in DMF solutions¹⁶. After the addition of NaBH_4 (4 mM - 250 mM) the height of the wave decreased in a non-linear fashion. The anodic wave was not observed even with a large excess of borohydride, an excess of bipyridine or by recording the polarographic limiting current with time. The results suggest that the mixed complex involving DMF and bipy shows a reduced stabilizing power and the Co(I) hydride complex is so unstable that it is not formed. Thus, water has an important effect on the formation of the intermediate Co(I) hydride complex (B) in a water-organic solvent.

The dependence of the reaction rate of the Co(II) complex with borohydride on temperature was also observed by using a polarographic experiment. The $0.51 \times 10^{-3} \text{ M } [\text{Co}(\text{bipy})_3]^{2+} + 75 \text{ mM NaBH}_4$ solution showed cathodic wave (-1.18 V) at 10°C or 21°C and an anodic wave (-1.18 V) at 25°C . With a less concentrated $[\text{Co}(\text{bipy})_3]^{2+}$ solution (0.31 mM) the composite wave was obtained at 21°C . The experimental data confirmed that the reducing ability of the borohydride solution is diminished at low temperatures. According to the mechanism proposed, lowering the temperature of the reaction reduces the rate of the formation of $[\text{CoH}(\text{bipy})_2]^0$ (Reaction 2).

Pulse polarography experiments

The normal pulse polarograms (NPP) and reverse pulse polarograms (RPP) obtained from a $1 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+}$ solution at different NaBH_4 concentrations (4 mM to 250 mM) showed only a small peak in NPP and RPP, which is typical of the adsorption phenomenon at the dropping mercury electrode^{17,18}. The polarograms correspond to

weak adsorption of both product and reactant on the electrode surface¹⁸. The occurrence of adsorption can be best observed when chloride is used as the supporting electrolyte.

The reversibility of the electrode process concerning $[\text{Co}(\text{bipy})_3]^{2+}$ solution at different NaBH_4 concentrations was verified by normal pulse polarography. The dependence between current and $t_m^{-1/2}$ (t_m = measuring time) for reversible systems must be linear at the potential picked in the polarographic wave¹⁹. The currents at different pulse widths are shown in Figs. 5, 6 and 7. The $1.0 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+} + 4.0 \text{ mM NaBH}_4$ solution presents reversible behavior (Fig. 5). The wave of the $1.0 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+} + 50 \text{ mM NaBH}_4$ solution (Fig. 6) is almost independent of the pulse width at $E_{1/2}$ and $E_{1/4}$. The I vs. $t_m^{-1/2}$ curve for the anodic wave of $1.0 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+} + 250 \text{ mM NaBH}_4$ solution are independent of the pulse widths at $E_{3/4}$, $E_{1/2}$ and $E_{1/4}$ (Fig. 7). Thus, the limiting

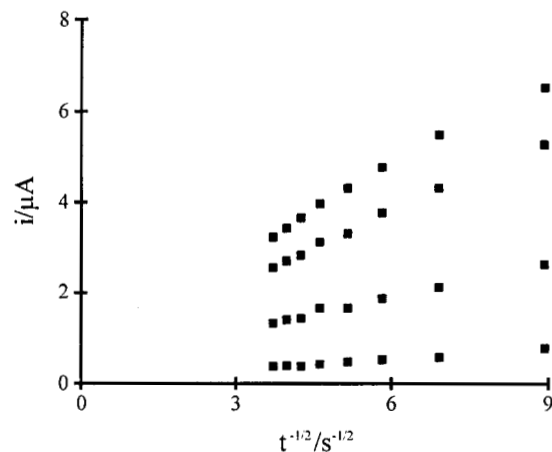


Figure 5. Dependence of the current on the measuring time of $1 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+} + 4.1 \text{ mM NaBH}_4$.

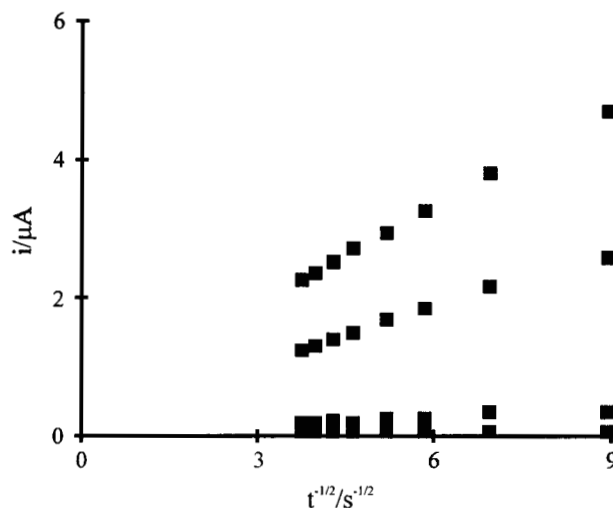


Figure 6. Dependence of the current on the measuring time of $1 \text{ mM } [\text{Co}(\text{bipy})_3]^{2+} + 50 \text{ mM NaBH}_4$.

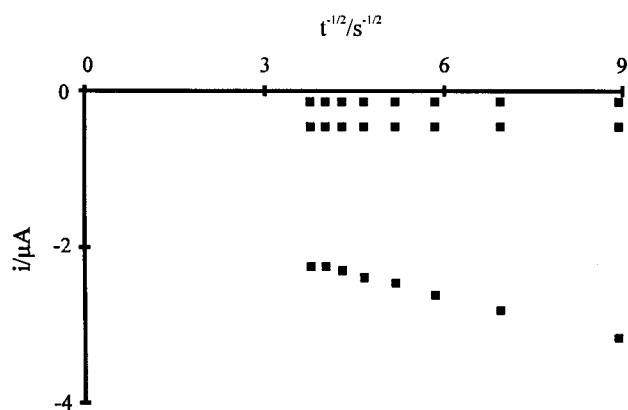


Figure 7. Dependence of the current on the measuring time of 1 mM $[\text{Co}(\text{bipy})_3]^{2+}$ + 250 mM NaBH_4 .

current is diffusion controlled, but currents at more positive potentials are kinetically controlled.

The analysis of the polarographic wave of 1.0 mM $[\text{Co}(\text{bipy})_3]^{2+}$ + 4.0 mM NaBH_4 solutions obtained under suitable conditions was performed in order to obtain the number of electrons involved in the electrochemical process. The value of n obtained by means of the Cottrell equation^{20,21} is 0.86, confirming the mechanism proposed.

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References

1. Vlcek, A.A. *Nature* **1957**, *180*, 573.
2. Bhayat, I.I.; McWhinnie, R.W. *J. Organometal. Chem.* **1972**, *46*, 159.

3. Mestroni, G.; Camus, A.; Cocevar, C. *J. Organometal. Chem.* **1971**, *29*, C17.
4. Camus, A.; Cocevar, C.; Mestroni, G. *J. Organometal. Chem.* **1972**, *39*, 355.
5. Cotton, A.F.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1980; p 766.
6. Kanai, H.; Yamamoto, N.; Kishi, K.; Mizuno, K.; Tarama, K. *J. Catal.* **1982**, *73*, 228.
7. McCue, P. J. *Coord. Chem. Rev.* **1973**, *10*, 265.
8. Burstall, H.F.; Nyholm, R.S. *J. Chem. Soc.* **1952**, 3570.
9. Wiberg, E.; Amberger, E. *Hydrides*; Elsevier: New York, 1971.
10. Waind, M.G.; Martin, B. *J. Inorg. Nucl. Chem.* **1958**, *8*, 551.
11. Mikheeva, L.V.; Konoplev, N.V. *Zhur. Neorg. Khim.* **1964**, *9*, 668.
12. Saji, T.; Aoyagui, S. *J. Electroanal. Chem.* **1975**, *60*, 1.
13. Mestroni, G.; Camus, A.; Mestroni, E. *J. Organometal. Chem.* **1970**, *24*, 775.
14. Cotton, A.F. *Inorg. Synt.* **1972**, *13*, 177.
15. Cotton, A.F. *Inorg. Synt.* **1980**, *20*, 208.
16. Fungaro, A.D.; Tokoro, R. *J. Braz. Chem. Soc.* **1995**, *6*, 23.
17. Barker, C.G.; Bolzan, A. *J. Frezenius Z. Anal. Chem.* **1966**, *216*, 215.
18. Flanagan, B.J.; Takahashi, K.; Anson, C.F. *J. Electroanal. Chem.* **1977**, *85*, 257.
19. Oldham, B.K.; Parry, P.E. *Anal. Chem.* **1970**, *42*, 229.
20. Parry, P.E.; Osteryoung, A.R. *Anal. Chem.* **1965**, *37*, 1634.
21. Delahay, P. *New Instrumental Methods in Electrochemistry*; Interscience: New York, 1980; p 23.

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