VOLTAMMETRIC STUDIES OF THE Co(II)-TRIS(HYDROXYMETHYL)-AMINOMETHANE AND SODIUM PERBORATE VOLUMETRIC CATALYTIC SYSTEM

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Received August 31, 2009
Accepted November 14, 2009

Dedicated to the 50th anniversary of awarding the Nobel Prize to Professor Jaroslav Heyrovský.

It has been shown that in the tris(hydroxymethyl)aminomethane (THAM)/HCl buffer, Co(II) ions catalyze the oxidation of THAM by sodium perborate. The reaction occurs at boiling temperature, and the product of the catalytic THAM oxidation, tris(hydroxymethyl)-nitrosomethane, gives a well-defined quasireversible cathodic wave preceding that of the Co(II) ions by about 160 mV. The voltammetric responses of this product are proportional to the amount of sodium perborate and to the concentration of Co(II) ions. In the volumetric catalytic system of Co(II) ions/THAM/sodium perborate, the sensitivity of the determination of Co(II) is increased by one to two orders of magnitude, depending on the voltammetric technique used. Prior to the detection of tris(hydroxymethyl)nitrosomethane, EDTA was added to the solution to form voltammetrically inactive complexes with Co(II) and other interfering ions. Therefore, this method may be applied for the determination of Co(II) ions at low concentrations in the presence of a large excess of interfering ions, in particular Ni(II) and Zn(II).

Keywords: Volumetric catalytic system; Tris(hydroxymethyl)aminomethane (THAM); Sodium perborate; Cobalt; Voltammetry; Electrochemistry.

The catalytic systems applied in voltammetry may be divided into several groups[1–6]. In the system of the first kind, a catalytic reaction is triggered by changes in the oxidation state of metal ions such as Fe(III), Cr(III) and V(IV) in the cycle, viz. reduction of metal ions at the cathode and oxidation of the product of the electrochemical reduction by an oxidizing agent. In systems of the second kind, the catalytic reaction occurs in a different cycle, viz. the formation of a composite complex of an oxidizing agent with

Collect. Czech. Chem. Commun. 2009, Vol. 74, Nos. 11–12, pp. 1715–1725

doi:10.1135/cccc2009111

complexes of metal ions such as Co(II) or V(IV), followed by its electrochemical reduction. For some complexes of Cr(III), both kinds of catalytic reactions occur. These systems have been called composite catalytic systems.

The electrochemical properties and applications of catalytic systems in electroanalysis were discussed and reviewed by Turyan et al.[7], Czae and Wang[8], Bobrowski and Zarębski[4–6], and Banica and Ion[9]. In the vast majority of cases, catalytic reactions occur at the surface of the working electrode, usually a mercury electrode. Voltammetric techniques have also been applied in volumetric catalytic systems, i.e., in cases when catalytic reactions take place in the bulk solution. These reactions, induced by some ions, were applied for their indirect determination at very low concentrations.

Generally, these systems may be divided in two groups. In the first group, the ions, usually complexed, induce a reaction between substances present in the solution. The progress of the reaction is monitored by using a selected analytical method. The analytical responses of the substrate (reagent) or the product enable us to determine the concentration of the catalyst, i.e., the metal ion, by means of a proper kinetic equation[10,11]. In the second group, the catalytic reaction induced by the metal ions occurs during a certain period of time, very often at high temperature, e.g. during boiling. When completed, the final product of this reaction is determined.

In most cases, photometric techniques are applied for monitoring of temporal changes in the concentration of the substrate/product among the first group, or the concentration of the final product of the catalytic reaction among the second group. However, when the substrate/product of the catalytic reaction is electrochemically active, voltammetric methods may also be applied. For example, traces of *ortho*-phenylenediamine were determined by monitoring its oxidation by Cu(II) ions[12]. The catalytic activity of W(VI) in the reaction between Methyl Red and Ti(III) was used for the quantitative determination of its traces[13]. Also, Rh(III) was determined from its catalytic activity in the reaction between Basic Blue 12 and IO_4^- ions[14]. In these studies, fast voltammetric techniques, such as linear scan oscillopolarography or fast linear scan voltammetry, were applied.

Examples of the second kind of volumetric catalytic systems include: (i) chlorine as catalyst of the oxidation of Methyl Orange[15], (ii) traces of Fe(III) as a catalyst of the oxidation of Acid Chrome Blue K by BrO_3^- [16], (iii) Cu(II) as a catalyst of the reaction between *ortho*-phenanthroline and ascorbic acid[17], and NO_2^- ions as a catalyst of the oxidation of 1-amino-2-naphthol-4-sulfonic acid[18]. Any voltammetric technique may be used to detect the final products of the volumetric catalytic reactions of the second kind.

An interesting example of the application of volumetric catalysis was the tensammetric determination of traces of Fe(III) that catalyze oxidation of 5-aminosalicylic acid by BrO_3^- ions, whereby exploiting the adsorption of the product of this reaction (5-aminoiminosalicylic acid) on the surface of the mercury electrode[19,20].

This work presents the results of voltammetric studies of a new volumetric catalytic system, in which the complex of Co(II) ions with tris(hydroxymethyl)-aminomethane (THAM) catalyzes oxidation of THAM by sodium perborate.

EXPERIMENTAL

Reagents

The chemicals used were of AR grade. Sodium perborate, $NaBO_2 \cdot H_2O \cdot 3H_2O$, prepared from sodium metaborate and hydrogen peroxide[21], was stored in a refrigerator to prevent decomposition.

The solution of 0.05 M sodium perborate was prepared prior to use by dissolving an appropriate amount of $NaBO_2 \cdot 3H_2O$ in water at room temperature. The exact concentration of sodium perborate was determined by means of titration with $KMnO_4$.

Measurements

Sampled direct current (DC), differential pulse (DP) and normal pulse (NP) polarograms were recorded by using a pulse polarograph PP-04 (Unitra Telpod, Krakow, Poland) and an XY recorder TRP 437 (Sefram, Paris, France), at a dropping mercury electrode (drop time 2 s, surface area 2.35 mm^2) and scan rate of 0.092 V min^{-1}. The alternating current (AC) polarograms were recorded at scan rate of 0.1 V min^{-1} and pulse amplitude of 10 mV with a phase-sensitive adapter[22] connected to an OH-105 Polarograph (Radelkis, Budapest, Hungary). Fast linear potential sweep (LPS) polarograms were recorded at scan rate of 1 V s^{-1} with a OP-4 Digiscope polarograph (Unitra Telpod, Krakow, Poland).

All voltammetric experiments were carried out with an Autolab PGSTAT 20 equipped with the GPES software package (Eco Chemie, Utrecht, The Netherlands). The electrochemical cell was equipped with a control growth mercury drop electrode (MTM Krakow, Poland) with surface area of 4.23 mm^2 as the working electrode used in the HMDE mode, Ag|AgCl (3 M KCl) as the reference electrode and platinum wire as the auxiliary electrode.

The pH values were determined by a glass electrode and a pH-meter N 517 (Mera Elwro, Wroclaw, Poland).

UV-Vis spectra were recorded with a spectrophotometer Lambda 10 (Perkin Elmer) in quartz cuvettes.

Procedure

An adequate amount of the standard solution of Co(II) ions was transferred to a 100-ml glass beaker, followed by addition of the buffer (1 M THAM/appropriate amount of HCl) (10 ml) and 0.05 M sodium perborate (10 ml). The solution was kept at boiling temperature for 10 min. Then, 0.05 M Na_2SO_3 (5 ml) was added and the beaker was cooled. The solution was transferred to a volumetric flask containing 0.2 M EDTA (0.5 ml) and diluted with deionized water to reach the total volume of 50 ml. An aliquot of this solution was transferred to a voltammetric vessel and the pH was fixed at the desired value. Finally, argon was passed through the solution for 7 min before polarograms or voltammetric curves could be recorded between –0.8 and –1.2 V.

RESULTS AND DISCUSSION

Mechanistic Studies

The preliminary investigations of polarographic and voltammetric properties of Co(II) ions in the supporting electrolyte of the THAM/HCl buffer have shown that after adding sodium perborate and subsequently boiling the solution for 10 min, a new polarographic peak preceding that of the reduction of the Co(II) ions to Co(0) appeared at ca. –0.9 V (Fig. 1, curve 1). This peak is several times higher than that for the Co(II) ions. Addition of a strongly complexing agent, such as EDTA, does not affect the current intensity and the potential of the new peak, while it does affect the original Co(II) response, which disappears entirely (Fig. 1, curve 2). The peak current of the product of the volumetric catalytic reaction between THAM and perborate, induced by Co(II) ions, increases with the concentration of sodium perborate.

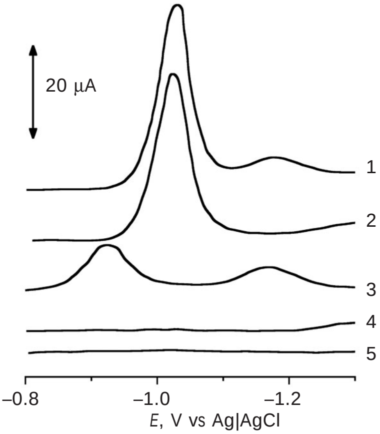

FIG. 1

DP polarograms: 1 5×10^{-6} M Co(II) in the supporting electrolyte 0.1 M THAM/2×10^{-3} M sodium perborate/5×10^{-3} M Na_2SO_3; 2 the same solution as 1 and 2×10^{-3} M EDTA; 3 5×10^{-6} M Ni(II)/Co(II) in the supporting electrolyte 0.1 M THAM; 4 the same solution as 3 and 2×10^{-3} M EDTA; 5 pure supporting electrolyte 0.1 M THAM/2×10^{-3} M EDTA/5×10^{-3} M Na_2SO_3. Solutions (1), (2): 10 min boiling. ΔE_{DP} = 20 mV, sampling time 40 ms

Boiling the solution is necessary not only in order to produce a voltammetrically active compound by the oxidation of THAM, but also to decompose the excess of sodium perborate. In the THAM/HCl buffer, sodium perborate yields broad polarographic curves, interfering with those of the product of catalytic oxidation of THAM. Larger amounts of sodium perborate were not decomposed completely, even after 10 min of boiling, and the addition of Na_2SO_3 was necessary to remove the rest of sodium perborate. To avoid the overlap of the diffusion wave of Co(II) ions with that of the product of catalytic oxidation of THAM, especially when the polarographic techniques DCP and NPP with wave responses were employed, EDTA was added to the solution prior to the measurement. EDTA forms strong complexes with Co(II) ions, as well as with other interfering ions, such as Ni(II) and Zn(II). These complexes become polarographically inactive within the range of potentials in which the voltammetric curves of the product of the catalytic oxidation of THAM are recorded.

Figure 2a presents the cyclic voltammetric curve of the product of the oxidation of THAM by sodium perborate, catalyzed by 1×10^{-6} M Co(II), recorded at 100 mV s^{-1}. The difference between the cathodic and anodic peak potentials amounts to 88 mV, which means that the reduction of the product of catalytic oxidation of THAM is quasireversible. An inspection of the relation between the forward and backward square wave (SW) voltammetric

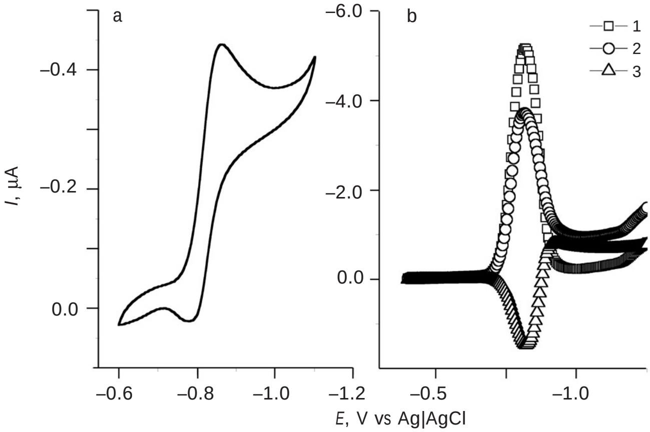

FIG. 2

The cyclic LSV (a) and SWV curves (b, curves 1–3) of the product of catalytic reaction in the solution containing 1×10^{-6} M Co(II) in the supporting electrolyte 0.2 M THAM/1×10^{-2} M sodium perborate/5×10^{-3} M Na_2SO_3/2×10^{-3} M EDTA; 10 min boiling. a Scan rate 100 mV s^{-1}. b Curves 1–3: net, forward and backward of SWV constituents, respectively. ΔE_{SW} = 50 mV, f = 50 Hz, step increment E_s = 5 mV components (Fig. 2b, curves 2, 3) also indicates that the reduction process is not completely reversible. This conclusion is also confirmed by the well-defined but slightly asymmetrical AC polarogram with a peak width $W_{1/2}$ = 88 mV, shown in Fig. 3.

To identify the product of the catalytic reaction, its UV-Vis absorption spectra were recorded. They show a band located at λ_{max} = 273 nm. This band is characteristic for organic compounds containing the nitroso functional group, for example tris(hydroxymethyl)nitrosomethane, $(HOCH_2)_3C{-}N{=}O$ [23].

It can be concluded that the catalytic reaction between THAM and perborate can be expressed by the following equation:

$$(HOCH_2)_3C{-}NH_2 + 2\ BO_2H_2O_2^- \xrightarrow{\text{Co(II)/Co(III)}} (HOCH_2)_3C{-}NO + 2\ BO_2^- + 3\ H_2O\ . \quad (1)$$

It follows from the relationship between the peak potential and pH, shown in Fig. 4 that protons participate in the electrode reaction. Thus, it is most likely that the electrode reaction occurs according to the following equation:

$$(HOCH_2)_3C{-}NO + 2\ e + 2\ H^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (HOCH_2)_3C{-}NHOH\ . \quad (2)$$

The product of the electrochemical reaction (*2*) yields an anodic peak in cyclic voltammetry and an oxidation peak in square wave voltammetry (SWV) (see the backward curve 3 in Fig. 2b). This means that the electrochemical reduction of the product of the catalytic oxidation of THAM

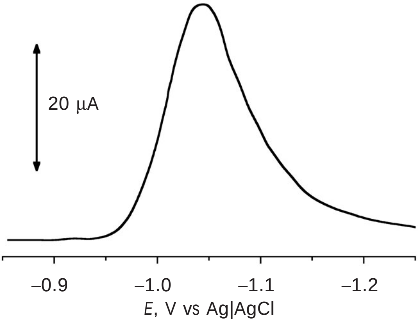

FIG. 3

AC polarogram of 5 × 10^{-6} M Co(II) in the supporting electrolyte 0.1 M THAM/5 × 10^{-3} M sodium perborate/5 × 10^{-3} M Na_2SO_3/2 × 10^{-3} M EDTA; 10 min boiling. ΔE_{SW} = 20 mV, f = 50 Hz does not lead to the restoration of the substrate of this reaction, i.e., THAM, which is electrochemically inactive, but to a partial reduction to $(HOCH_2)_3C–NHOH$.

Analytical Performance

The observed catalytic peak can be utilized for the indirect determination of Co(II) ions. The value and the shape of the observed catalytic signal depend on two factors:

(*1*) the experimental conditions for the catalytic reaction, such as the concentration of sodium perborate and Co(II) ions and the pH of the supporting electrolyte;

(*2*) the pH of the solution in which voltammetric measurements are carried out, and the voltammetric mode applied.

Figure 5 shows the dependence of the catalytic current on the concentration of sodium perborate. As can be seen from the presented plot, the concentration of sodium perborate is the key factor as far as the magnitude of the catalytic effect is concerned. The linear relationship between the catalytic current and the sodium perborate concentration was observed up to 1 × 10^{-2} M perborate, and this concentration was chosen as the optimum concentration for further experiments.

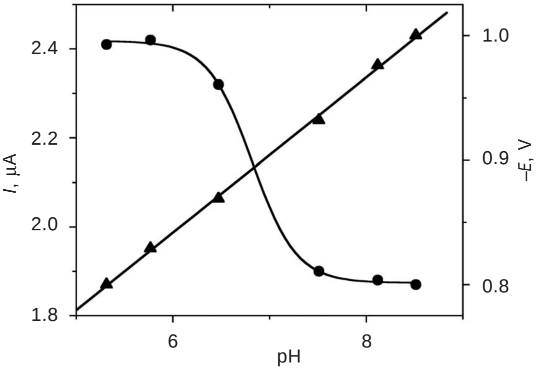

FIG. 4

Dependence of SWV peak current (●, left axis) and peak potential (▲, right axis) of the product of the catalytic reaction on pH of the solution containing 1 × 10^{-6} M Co(II) in 0.2 M THAM/1 × 10^{-2} M sodium perborate/5 × 10^{-3} M Na_2SO_3/2 × 10^{-3} M EDTA. Prior to voltammetric measurements, the solutions were boiled for 10 min, followed by addition of EDTA and Na_2SO_3. ΔE_{SW} = 50 mV, f = 20 Hz, step increment E_s = 5 mV

In the next set of experiments, the DP and SW voltammograms of the product of the THAM oxidation at pH 8.4 were recorded for various pH values to achieve the highest sensitivity of the voltammetric response. In the optimum pH range between 5.2 and 6.0, the variation of pH does not affect the height of the catalytic peaks significantly. For pH values between 6.2 and 7.3, the peak current decays considerably, and finally levels off in the range of 7.4–8.5 (Fig. 4). The optimum pH was found to be 5.8. As the pH increased, the peak potentials shifted linearly towards more negative potentials (Fig. 4) with the slope $\Delta E_p/\Delta pH$ equal to 63 mV/pH.

The sensitivity of the SW voltammetric response (f = 50 Hz) was about 3 times higher than that for the DPV technique. A comparison of the catalytic effects for different polarographic and LS voltammetric techniques, expressed as the ratio of the limiting current or the peak current of the product of the THAM oxidation to the corresponding values of the currents of the Co(II) reduction, is presented in Table I.

The values of the catalytic effects are similar for DC polarography, sample direct current (SDC) polarography and NP polarography, i.e., for the methods in which the reversibility of the reduction does not significantly influence the values of the limiting currents. Surprisingly, the high value

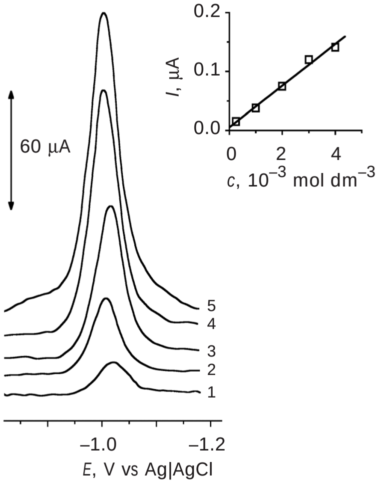

FIG. 5

DP polarograms of the product of the volumetric catalytic reaction in the solution containing 4×10^{-6} M Co(II)/0.1 M THAM and: 1 2.5×10^{-4}, 2 1×10^{-3}, 3 2×10^{-3}, 4 3×10^{-3}, 5 4×10^{-3} M sodium perborate. Inset: The dependence of the peak current on the perborate concentration. Prior to polarographic measurements, the solutions were boiled for 10 min, followed by addition of 2×10^{-3} M EDTA and 5×10^{-3} M Na_2SO_3. Pulse amplitude 20 mV, sampling time 40 ms for the catalytic effect observed in ACP can be explained by the irreversibility of the reduction of the Co(II) ions, and, therefore, the low sensitivity of its ACP response.

In consecutive experiments, the catalytic reaction between THAM and perborate in the presence of the Co(II) ions was induced in solutions of pH, ranging between 7.2 and 10.7. After 10 min of boiling, interrupting the re-

TABLE I
The ratio of the catalytic currents of the product of the THAM oxidation to the signal of Co(II)

Method	$i_{\mathrm{THAM}}{}^{a}/i_{\mathrm{Co}}{}^{b}$
DC polarography	14.96
DC tast polarography	13.86
CV voltammetry (cathodic peak)	8.78
AC polarography	557.7
NP polarography	12.72
DP polarography	26.20

[a] Composition of the solution: 5 × 10^{-6} M Co(II)/0.1 M THAM/5 × 10^{-3} M sodium perborate/ 5 × 10^{-3} M Na_2SO_3/2 × 10^{-3} M EDTA (10 min of boiling). [b] Composition of the solution: 5 × 10^{-6} M Co(II)/0.1 M THAM.

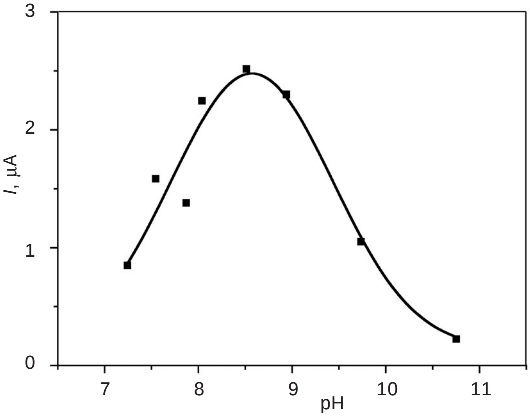

FIG. 6
Effect of pH on the efficiency of the catalytic reaction between THAM and perborate in the presence of 1 × 10^{-6} M Co(II) as the catalyst. Composition of the solution: 0.2 M THAM/1 × 10^{-2} M sodium perborate/5 × 10^{-3} M Na_2SO_3/2 × 10^{-3} M EDTA. ΔE_{SW} = 50 mV, f = 50 Hz, step increment E_s = 5 mV

action by addition of Na_2SO_3 and cooling the solutions, their pH was fixed to 5.8 and SW voltammograms were recorded. As can be seen from Fig. 6, the catalytic effect is pH-dependent. The highest efficiency of the catalytic reaction was achieved at pH 8.5. The increase in the temperature of the solution caused an increase in the voltammetric response. The temperature coefficient for DCP was found to be 1.87% with regard to the value at 20 °C.

For a constant concentration of sodium perborate in the solution, viz. 1×10^{-2} mol dm^{-3}, the SWV catalytic responses were proportional to the concentration of Co(II) within the investigated concentration range 5×10^{-8}–1×10^{-6} mol dm^{-3}, with a slope 8.5 μA μM^{-1}. The relative standard deviation for eight replicate measurements of blank was equal to 0.4%. The limit of Co(II) detection restricted by blank was 7.5×10^{-8} mol dm^{-3}. Further purification of the applied reagents (i.e., THAM and sodium perborate) should allow for lowering the detection limit.

To determine the Co(II) traces in the presence of a large excess of interfering ions, typically Ni(II) and Zn(II), after interrupting the catalytic reaction, an addition of EDTA into the solution is recommended in order to bind them in complexes. In the presence of EDTA the interfering peaks disappear.

Although the proposed polarographic method is less sensitive than the catalytic adsorptive stripping voltammetric procedures with dioximes and nitrite[24], there are two advantages of the proposed method. First, it offers a relatively low detection limit in comparison with other polarographic methods. Second, a very good selectivity against most coexisting species can be achieved.

Financial support from the Polish Ministry of Science and Higher Education (Project No. N507063 32/1767) is gratefully acknowledged.

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