

**SOME CONSIDERATIONS ON THE ONE-ELECTRON ELECTROCHEMICAL  
REDUCTION OF NITROPRUSSIDE. THE USE OF COULOMETRY IN THE ANALYSIS  
OF THE REDUCTION PROCESS.**

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**Abstract**

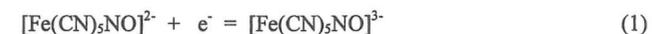
The one-electron electrochemical reduction of the nitroprusside ion (NP) in aqueous solution of different pH was studied by cyclic voltammetry and by coulometry. The UV-VIS spectra of the electrolysis final solutions show conclusively that, at pH 5.1, the ion  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  is the final product of the first one-electron reduction of NP although it decomposes through some process favoured by the decrease of pH. Also, the analysis of the cyclic voltammograms and of the curves electrolysis current vs. charge for the pH range under consideration shows that there is a chemical reaction, involving  $\text{H}^+$ , following the electron transfer step. Indeed, HCN was detected as a product of the first one-electron reduction of NP and at pH 3.0, the variation of pH at the end of the electrolysis was evaluated and it corresponds to the expected for the consumption of 1  $\text{H}^+$  in order to produce 1 HCN. Hence we conclude that  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  is the final product of the 1-electron electrochemical reduction of NP.

**Keywords:** Nitroprusside; electrochemical reduction;  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ ; coulometry

**INTRODUCTION**

The redox chemistry of the nitroprusside ion (NP),  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ , has been the subject of great interest for more than three decades. The study of the reactions of coordinated  $\text{NO}^+$  is of major importance not only from the physico-chemical standpoint but also as a basis for the understanding of the physiological and biochemical role of nitric oxide. [1]

There has been some disagreement about the identity of the product of the 1-electron reduction of NP to which several formulations have been assigned, e.g.  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ ,  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ ,  $[\text{Fe}(\text{CN})_5\text{NOH}]^{2-}$  and  $[\text{Fe}(\text{CN})_5\text{NO}_2]^{4-}$ . Studies of the reduction process by several methods including crystallographic techniques, [2] EPR, [3] and pulse-radiolysis / UV-VIS spectroscopy [4] proved that the final 1-electron product is the blue penta-coordinated ion  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  (more important band,  $\lambda_{\text{max}} = 615 \text{ nm}$ ,  $\epsilon_{\text{max}} = 380 \text{ M}^{-1}\text{cm}^{-1}$ ). However, the initial reduction product must be  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  (more important band,  $\lambda_{\text{max}} = 345 \text{ nm}$ ,  $\epsilon_{\text{max}} = 3500 \text{ M}^{-1}\text{cm}^{-1}$ ), in which the  $\text{NO}^+$  ligand has been reduced to  $\text{NO}^0$ . The ion  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  undergoes a unimolecular decay to give the ion  $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$  by releasing the axial cyanide ligand. [4]



Nevertheless, the product generated polarographically at mercury electrodes in acidic solution was proposed to be the protonated ion  $[\text{Fe}(\text{CN})_5\text{NOH}]^{2-}$ . [5, 6] Recent electrochemical studies did not clarify this question. [7] Our recent work involves studies of the electrochemistry of NP in acidic solution. [8] Because the nature of the first one-electron electrochemical reduction product still needs clarification we decided to examine more intensively the 1-electron reduction process of NP in acidic solution.

In the present work we use coulometric analysis to compare the reduction process in alkaline and acidic media (pH values of 7.7, 5.1 and 3.0). The electrolysis final solutions are analysed by UV-VIS spectroscopy. The amount of HCN released during the electrolysis process is determined. At pH 3.0 also the amount of H<sup>+</sup> consumed is estimated. Our main goal is to verify if, at all pH values, [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> is the unique product of the 1-electron electrochemical reduction of NP.

**EXPERIMENTAL**

Sodium nitroprusside dihydrate (Panreac), boric acid (Panreac), orthophosphoric acid (Riedel-deHaen), acetic acid (Merck), sodium hydroxide (Merck), hydrochloric acid (Merck) were of analytical-reagent grade. A HCl solution or Britton-Robinson (BR) buffers were used as electrolyte solutions, the pH being adjusted with 1 mol dm<sup>-3</sup> NaOH. Deionized water (Milli-Q - Millipore system) was used to prepare all solutions.

Bulk electrolysis with coulometric analysis experiments were performed using a PAR 279A digital coulometer connected to a PAR 363 potentiostat/galvanostat. The working electrode was a mercury pool, the auxiliary electrode was a Pt coil and the reference electrode was a SCE. The electrolysis solution was continuously purged with N<sub>2</sub>. For the determination of HCN, a 0.1 moldm<sup>-3</sup> NaOH solution trap with 3 collection flasks in series was connected to the electrolysis cell. The concentration of HCN collected as CN<sup>-</sup> was determined by differential pulse voltammetry (DPV). The standard addition method was used (KCN standard solution, 7.79 × 10<sup>-4</sup> mol dm<sup>-3</sup>). The amount of H<sup>+</sup> consumed during the electrolysis was estimated by measuring the pH at the beginning and at the end of the electrolysis.

Cyclic voltammetric and DPV experiments were performed using a BAS 100B/W electrochemical analyser connected to a PAR 303A mercury electrode stand in the HMDE mode (medium drop size). The auxiliary electrode was a Pt wire and the reference electrode was Ag/AgCl (saturated KCl). All solutions were deoxygenated with nitrogen for 4 minutes before the electrochemical measurements.

UV-VIS absorption spectra were obtained using a Shimadzu UV-2101PC UV-VIS spectrophotometer.

pH measurements were made with a combined pH-reference electrode and an Anatron pH300 pH meter. All experiments were carried out at room temperature. Both the voltammetric cell and the electrolysis cell were wrapped in aluminium foil to prevent light degradation of NP. All potentials quoted are relative to the Ag/AgCl (saturated KCl) reference electrode.

**RESULTS AND DISCUSSION**

Fig. 1 displays typical cyclic voltammograms of 1.2 × 10<sup>-3</sup> mol dm<sup>-3</sup> NP solutions at different pH values, obtained at 50 mV s<sup>-1</sup>. At pH 7.7 the voltammetric characteristics point to the occurrence of an 1-electron reversible process, as expected (see above, eqn. 1). In acidic solutions the anodic peak decreases gradually as pH decreases and disappears for pH ≤ 4. Moreover, the cathodic peak potential shifts negatively with increasing scan rate (result not shown) as expected for an EC process and at pH 4 it shifts -0.024 V per 10 fold increase in the scan rate, indicating that the system is in the pure kinetic region. [9] These results are in accordance with the occurrence of a pH-dependent chemical reaction following the 1-electron transfer. This might mean that [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> is being formed by release of CN<sup>-</sup> (see above, eqn.2). By decreasing pH the formation of HCN takes place, leading to an increase of the rate constant of reaction 2. However, just from the analysis of these cyclic voltammetric results the occurrence of a protonation reaction leading to the formation of [Fe(CN)<sub>5</sub>NOH]<sup>2-</sup>, the species proposed by Masek and col. [6], can not be neglected.

In order to compare the reduction process both in alkaline and acidic solutions, bulk electrolysis experiments with coulometric analysis were carried out at the potential of the diffusion plateau for the first 1-electron reduction process, -0.36 V. The main goal was to analyse the reduction

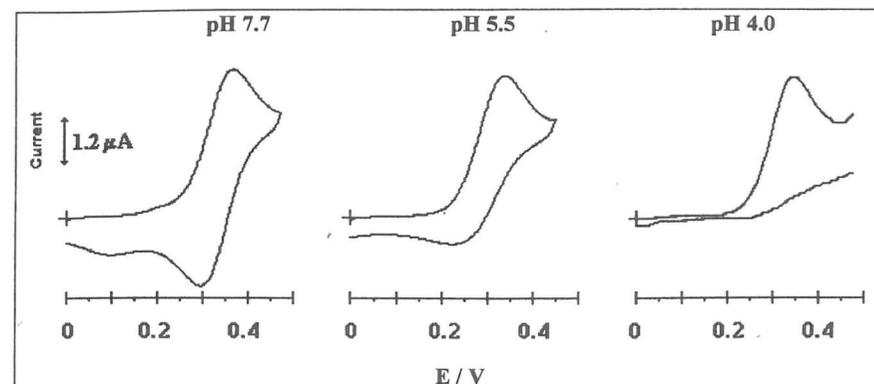


Fig. 1. Cyclic voltammograms of 1.2 × 10<sup>-3</sup> mol dm<sup>-3</sup> NP solutions (BR buffers of different pH value). Initial potential, 0 V; scan rate, 0.05 Vs<sup>-1</sup>.

products, namely the existence of [Fe(CN)<sub>4</sub>NO]<sup>2-</sup>. On the other hand, if no [Fe(CN)<sub>5</sub>NOH]<sup>2-</sup> is being generated, no HCN will be released from the primary reduction product, [Fe(CN)<sub>5</sub>NO]<sup>3-</sup>. Hence, a HCN trap was connected to the electrolysis cell in order to collect any HCN produced during the electrolysis. At pH 3.0, also the amount of H<sup>+</sup> consumed in the electrolysis reaction was estimated by measuring pH before and after the electrolysis. In this particular experiment a HCl solution was used as the electrolyte solution. Table 1 presents the results obtained from the electrolysis experiments and Fig. 2. displays the UV-VIS spectra of the final electrolysis solutions. As we can see from table 1 the reduction of NP is always an 1-electron reaction, independently of the pH value. At pH 7.7 the solution was green and the UV-VIS spectrum shows clearly the absorption bands of both the initial reduction product, [Fe(CN)<sub>5</sub>NO]<sup>3-</sup>, at 343 nm and the penta-coordinated ion [Fe(CN)<sub>4</sub>NO]<sup>2-</sup>, at 617 nm. Moreover, HCN was released from the electrolysis solution: the value of 0.3 indicates that approximately 30% of [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> was generated from the initial reduction product and therefore the final solution must contain a mixture of both ions. At pH 5.5, the UV-VIS data and the amount of HCN collected are in agreement with the complete conversion of [Fe(CN)<sub>5</sub>NO]<sup>3-</sup> into the blue species [Fe(CN)<sub>4</sub>NO]<sup>2-</sup>. However, the [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> solution is unstable and the blue colour vanishes in about 15 minutes. Indeed, Masek and col.[6] proposed that the ion [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> generated in alkaline solutions, decomposes due to the slow loss of CN<sup>-</sup> giving a tricyano complex, [Fe(CN)<sub>3</sub>NO]<sup>2-</sup>. On the other hand, decomposition of [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> to give ferrocyanide [3b] or even Prussian blue [5] were also reported.

**Table 1.** Determination of the number of electrons, *n*, by controlled potential coulometry at the potential of the first 1-electron reduction process. Determination of the ratio between the amount of H<sup>+</sup> consumed and the initial amount of NP, rH<sup>+</sup>, and of the ratio between the amount of HCN produced and the initial amount of NP, rHCN.

pH	7.7	5.1	3.0
amount of NP /mol	3.11 × 10 <sup>-5</sup>	1.53 × 10 <sup>-5</sup>	3.01 × 10 <sup>-6</sup>
Q /C	3.060	1.490	0.308
<i>n</i>	1.02	1.01	1.06
solution colour	green	blue	colourless
rH <sup>+</sup>	-	-	0.9 (N=2)
rHCN*	0.3 (N=1)	1.0 (N=1)	0.9 (N=2)

\*estimated considering the loss of HCN through the experimental set-up

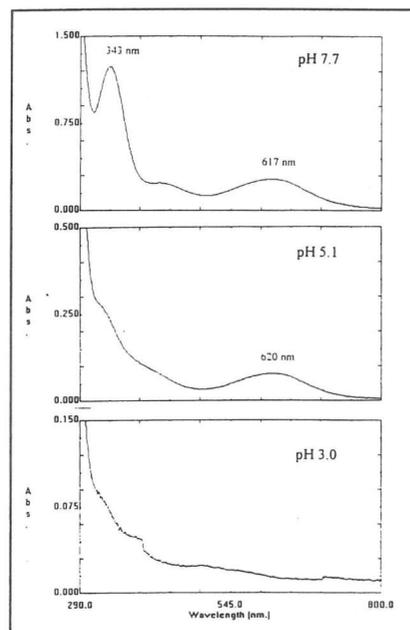


Fig. 2. Absorption spectra of the electrolysis final solutions at different pH. Initial concentration of NP (mol dm<sup>-3</sup>): 2.0×10<sup>-3</sup> at pH 7.7; 1.0×10<sup>-3</sup> at pH 5.1 and 2.0×10<sup>-4</sup> at pH 3.0

and charge. The occurrence of a rather fast chemical step following the electron transfer would not produce any evident distortion of the current vs. charge. In this situation the kinetics of the system would be dominated only by the electron transfer.

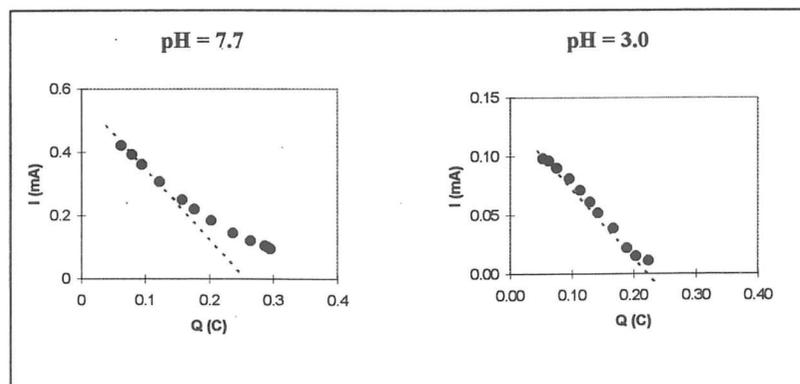


Fig.3. Plots of the current vs. charge for the electrolysis of 2.0×10<sup>-4</sup> mol dm<sup>-3</sup> NP solutions of different pH values.

In fact, at pH 3.0, the final electrolysis solution was colourless. Only for the 1×10<sup>-3</sup> moldm<sup>-3</sup> NP concentration level a pale blue colour was observed during the electrolysis, but the final solution had no distinguished colour. This is indeed indicative of some decomposition of the reduction product, which is easier in acidic solution. Still, the determination of HCN generated during the electrolysis at pH 3.0 points to a 100% production of [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> and the corresponding variation of pH point to a consumption of 0.9 protons *per* mol of NP. If the protonated ion [Fe(CN)<sub>5</sub>NOH]<sup>2-</sup> proposed by Masek and col. [6] was produced by protonation of the initial brown [Fe(CN)<sub>5</sub>NO]<sup>3-</sup>, then no HCN should be released.

Fig.3 shows plots of the current vs. charge for the electrolysis performed at pH 7.7 and 3.0. From these plots the number of electrons consumed in the reaction can also be evaluated by extrapolation of the plots to zero current and values ranging from 0.8 to 1.0 were obtained. The curve obtained at pH 7.7 presents deviation from linearity which accounts for the effect of a relatively slow chemical step after the electron transfer [9]. This behaviour agrees with what was expected by considering the occurrence of the slow release of CN<sup>-</sup> from the initial reduction product (eqn.2). At pH 3.0 there is an apparent linear relationship between current

The chemical step at pH 3.0 can be written as:



and this reaction will most probably involve the direct protonation of the leaving axial cyanide group [4].

### CONCLUSION

From our results we may conclude that [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> is the product of the first one-electron reduction of NP when generated electrochemically in acidic solution. The existence of [Fe(CN)<sub>5</sub>NOH]<sup>2-</sup> is unlikely. However, the stability of [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> in aqueous solution decreases markedly with decreasing pH. The identification of the degradation product(s) of [Fe(CN)<sub>4</sub>NO]<sup>2-</sup> in acidic solution was not yet achieved.

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