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Electrochemistry of the Nitroprusside Ion in Nonaqueous Solvents

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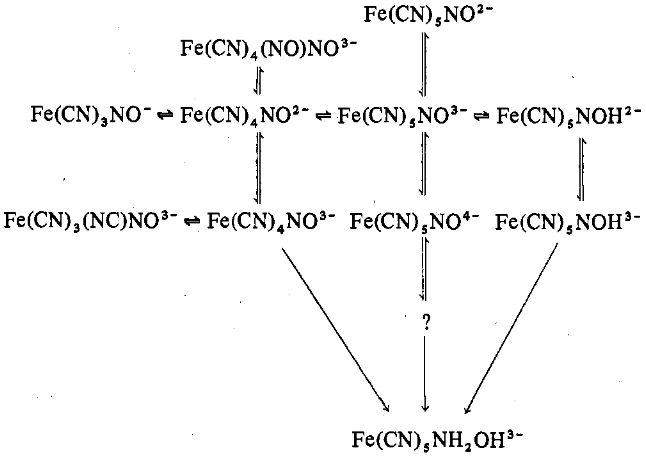
The electrochemical reduction of the pentacyanonitrosylferrate(II) anion has been studied in nonaqueous aprotic media by polarography, cyclic voltammetry, and coulometry. In contrast to results from aqueous solution, the initial one-electron reduction proceeds with a rapid loss of cyanide to give the blue five-coordinate tetracyanonitrosylferrate(I) anion. The tetracyanonitrosylferrate(I) anion undergoes a further reversible reduction and an oxidation which is reversible at fast sweep rates.

In recent years the chemistry, particularly the redox chemistry, of the nitroprusside ion, $Fe(CN)_5NO^{2-}$, has been the subject of widespread interest,[1–3] and the reduction processes have been studied by a variety of synthetic[4–7] and physical techniques, including EPR,[8–16] Mössbauer spectroscopy,[17] and crystallographic[18] and thermoanalytical[16] methods. These studies have demonstrated that there exist at least two products resulting from the one-electron reduction of $Fe(CN)_5NO^{2-}$, one blue and the other yellow-brown. There is disagreement in the literature as to the identity of these species, and among the formulations which have been proposed for the products of the one-electron reduction of $Fe(CN)_5NO^{2-}$ are $Fe(CN)_5NO^{3-}$, $Fe(CN_5NOH^{2-}$, $Fe(CN)_4NO^{2-}$, $Fe(CN)_5NO_2^{5-}$, $Fe(CN)_4(NC)NO^{3-}$, and $Fe_2(CN)_{10}^{6-}$. Most of the discussion has centered on the first two, with conflicting claims for their assignment to the blue or brown species. The electrochemical reduction of the nitroprusside ion in aqueous media has been investigated by several groups,[19–24] most recently by Masek and co-workers.[22–24] The latter studied the nitroprusside problem by a variety of electrochemical techniques, including polarography, cyclic voltammetry, and coulometry. Rather complex behavior was encountered in these investigations, wherein two successive reversible reductions at −0.36 and ∼−0.6 V were followed by an irreversible multielectron reduction at ∼−0.9 V. Whereas the total current was equivalent to the transfer of 4 e, only the initial reduction appeared to be a clean, well-behaved reduction process. To rationalize the results of these studies, a reduction sequence was proposed (Scheme I[24]). Characterization of the initial reduction process is of particular interest, since the products formed are those which have been examined by EPR and Mössbauer and electronic spectroscopy.

The species $Fe(CN)_5NO^{3-}$, $Fe(CN)_5NOH^{2-}$, and $Fe(CN)_4NO^{2-}$ are of interest as the species which have been proposed as the brown and blue nitroprusside reduction products. The complex reduction mechanism of nitroprusside in aqueous solution prompted the present investigation of the nonaqueous electrochemical behavior of this system, since the protonated product, $Fe(CN)_5NOH^{2-}$, is not expected to form in aprotic media. Tetraalkylammonium salts of the nitroprusside ion are soluble in a variety of nonaqueous solvents, including acetonitrile and dichloromethane, and the electrochemical behavior of the nitroprusside ion has been studied in these solvents using polarography, cyclic voltammetry, and exhaustive electrolysis at controlled potential. The results of these studies, supported by EPR and electronic spectroscopy, have elucidated some details of the reduction chemistry of the nitroprusside ion in nonaqueous solutions and are reported in this paper.

Scheme I. Reduction Scheme for Nitroprusside Ion in Aqueous Solutions[24]



Experimental Section

Tetra-*n*-butylammonium nitroprusside, $[N(C_4H_9)_4]_2Fe(CN)_5NO$, was prepared by metathesis of sodium nitroprusside with tetrabutylammonium bromide in water and was purified by recrystallizations from water. The tetrabutylammonium hexafluorophosphate, $N(C_4H_9)_4PF_6$, was purified by repeated recrystallizations from hot ethanol and was used throughout as the supporting electrolyte (0.1 M).

Electrochemical measurements were taken with a PAR 173 potentiostat in conjunction with a Hewlett-Packard 3300A function generator and recorded on a Hewlett-Packard 7001A X-Y recorder or a Tektronix 502A dual-beam oscilloscope equipped with a C-27 camera.

All experiments were carried out in solutions deoxygenated with nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen immediately before use. Eastman Spectrograde acetonitrile was used without further purification. Bulk electrolyses were carried out in a normal three-compartment cell using a mercury pool working electrode with a platinum gauze auxiliary electrode. All potentials are given relative to the aqueous saturated calomel electrode. Bulk electrolyses were considered complete when the limiting current

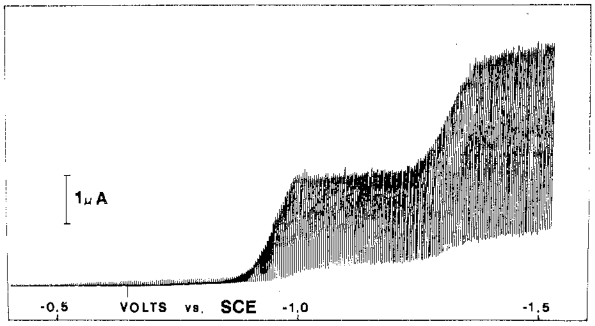


Figure 1. Polarogram of $(Bu_4N)_2Fe(CN)_5NO$ in CH_2Cl_2-Bu_4NPF_6.

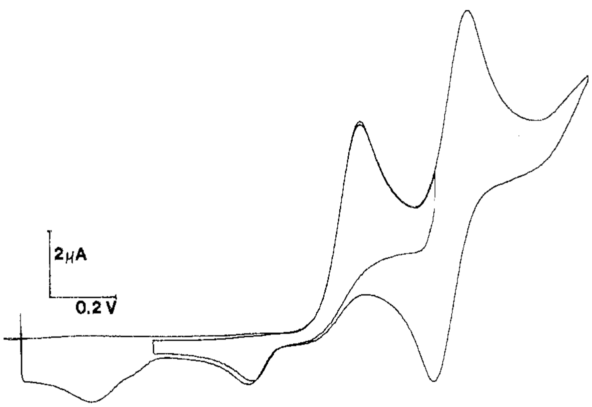


Figure 2. Cyclic voltammogram of $(Bu_4N)_2Fe(CN)_5NO$ in CH_2Cl_2-Bu_4NPF_6 at 80 mV/s.

dropped to less than 5% of the initial value.

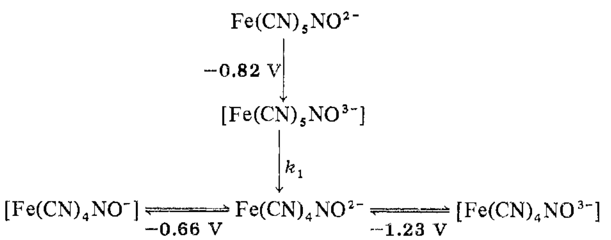
Electron spin resonance spectra were recorded on a Varian V-4502-9 system. Electronic spectra were taken with a Cary Model 14 spectrophotometer.

Results

Polarograms of $(Bu_4N)_2Fe(CN)_5NO$ in acetonitrile (Figure 1) or dichloromethane show two waves, in the vicinity of −0.9 and −1.3 V. In contrast to the behavior in aqueous solutions, the two reduction waves are of equal height and there is no indication of a third, irreversible multielectron reduction at more negative potentials. Polarographic results are consistent with the formulation that one electron is consumed in each wave. Evidence for this includes similarity of the diffusion coefficient constants, I_d, for the two waves (2.57 and 2.60 for the first and second waves, respectively) and the $E_{3/4} - E_{1/4}$ values of −60 and −80 mV. However, on addition of water to the acetonitrile solution, the two reduction waves are shifted to −0.48 and −0.80 V, while a multielectron reduction process appears at −1.89 V, consistent with earlier results in aqueous media.[24]

Cyclic voltammetry at a hanging mercury drop electrode (HMDE) shows that only the second reduction is chemically reversible (Figure 2). Attempts to detect reversibility on the first wave using scan rates of up to 50 V/s failed, demonstrating that the lifetime of the reduced nitroprusside ion, $Fe(CN)_5NO^{3-}$, is very short in these solvents (<10 ms). The potential of the peak cathodic current is sweep rate dependent but lies at −0.99 V at a sweep rate of 120 mV/s. The reverse scan on cyclic voltammetry at the first wave shows the oxidation waves (−0.66 and −0.20 V) which arise from products of the decomposition of $Fe(CN)_5NO^{3-}$. The oxidation at −0.66 V is irreversible except at high sweep rates (36 V/s) while the oxidation near −0.20 V is chemically reversible with a large peak separation (~200 mV). The height of the wave near −0.20 V is increased by the addition of tetra-*n*-butylammonium cyanide, and this wave is accordingly assigned to the oxidation of cyanide ion in solution.

Scheme II. Reduction Scheme for Nitroprusside Ion in Aprotic Solution



Exhaustive electrolysis at a mercury pool electrode at a potential on the diffusion-limited plateau for the first wave (−1.0 V) produces a blue solution. In this reduction *n*, the apparent number of electrons transferred, was found by coulometry to be 0.98 ± 0.05, confirming the conclusion that the first wave is an irreversible one-electron process. This blue solution was characterized by UV–VIS and EPR spectroscopy. The λ_{max} of 610 and 345 nm are similar to those reported for the complex previously thought to be $Fe(CN)_5NOH^{2-}$, which has now been reformulated as $Fe(CN)_4NO^{2-}$.[18] The EPR spectrum of the blue complex, at room temperature, shows an A_N = 14.6 G which is also similar to the results reported for "$Fe(CN)_5NOH^{2-}$" by Van Voorst and Hemmerich.[12]

A polarogram of the blue solution produced by the electrochemical reduction of $Fe(CN)_5NO^{2-}$ reveals two oxidation waves, one near −0.2 V which is poorly defined and another near −0.6 V which is obscured by a polarographic maximum. When several polarograms were taken in the course of the reduction, the gradual appearance of these oxidation waves could be monitored. In addition to these oxidation waves, the second reduction wave for the nitroprusside ion is still observed (at −1.23 V) with the same I_d and $E_{3/4} - E_{1/4}$ as found in the unreduced solution. All of these data are consistent with formulation of the blue product at $Fe(CN)_4NO^{2-}$, in which the original one-electron reduction of $Fe(CN)_5NO^{2-}$ has been followed by rapid loss of cyanide. On this basis, the wave found at −0.6 V in the blue solution can be assigned to the oxidation of the d^7 iron(I) species $Fe(CN)_4NO^{2-}$. Addition of phenol results in unchanged polarographic and EPR data for the square-pyramidal $Fe(CN)_4NO^{2-}$. Similarly, a polarogram of the nitroprusside ion in dichloromethane with phenol added showed no change from a polarogram without the proton donor. Presumably, $Fe(CN)_4NO^{2-}$ is not easily protonated in dichloromethane solution and there is no evidence for the occurrence of a protonated intermediate species such as $Fe(CN)_5NOH^{2-}$. $Fe(CN)_4NO^{2-}$ is somewhat air sensitive in solution and is slowly oxidized to a yellow diamagnetic species on exposure to air.

Bulk reduction on the plateau for the second wave appears to give a multielectron transfer with the appearance of several oxidation waves in the reduced system, none near the −1.23 V of the original wave. It is concluded that the initial reduction product, $Fe(CN)_4NO^{3-}$, decomposes in a further reaction, giving a green product. The greenish solution is quite air sensitive and is rapidly oxidized to a yellow-orange diamagnetic product. An attempt to characterize this green product by EPR using in situ electrolysis was unsuccessful, since the only signal observed is that assigned to $Fe(CN)_4NO^{2-}$.

Discussion

A reduction scheme for the nitroprusside ion in dichloromethane or acetonitrile is given in Scheme II. There are a number of differences between this scheme and that previously suggested for reductions in aqueous media (Scheme I[24]). The initially formed reduced nitroprusside $Fe(CN)_5NO^{3-}$ is unstable in aqueous solutions due to slow loss of cyanide, leading to formation of the tetracyano and tricyano complexes $Fe(CN)_4NO^{2-}$ and $Fe(CN)_3NO^{-}$, and also has been claimed to protonate to form the complex $\mathrm{Fe(CN)_5NOH^{2-}}$ and to form outer-sphere complexes of the sort $\mathrm{Fe(CN)_5NO{\cdot}M^{2-}}$ with alkali metal cations. However, in nonaqueous solutions we find no evidence of the stability of $\mathrm{Fe(CN)_5NO^{3-}}$, even with fast cyclic voltammetry. Furthermore, once the five-coordinate product $\mathrm{Fe(CN)_4NO^{2-}}$ is formed, it shows no tendency to undergo further loss of cyanide in aprotic media.

The blue complex as formed by reduction in dimethylformamide or in aqueous solutions at lower pH has been generally assigned the formulation $\mathrm{Fe(CN)_5(NOH)^{3-}}$. Our results cast doubt on the existence of such a species, since an apparently identical material is formed here under aprotic conditions. The pH dependence of the formation of the blue complex in aqueous solutions, which provides the basis for the formulation $\mathrm{Fe(CN)_5NOH^{3-}}$, is explicable in terms of a series of acid–base equilibria involving the weak acid HCN and the possibilities for direct protonation and hydrogen bonding involving nitrogen on the coordinated cyanide ligand. In fact, there is other evidence that the blue complex formed in dimethylformamide is $\mathrm{Fe(CN)_4NO^{2-}}$. Hockings and Bernal[10] examined EPR spectra of the blue product obtained by reduction of nitroprusside containing ^{13}C-labeled cyanide. They showed that the EPR spectrum exhibited only a series of five hyperfine lines arising from coupling to the four equivalent equatorial ligands, with no hyperfine lines arising from the axial cyanide, an observation consistent with the formulation $\mathrm{Fe(CN)_4NO^{2-}}$. It is of interest to compare these findings with the results for the reduction of other $\mathrm{d^6}$ nitrosyls obtained by Meyer and Callahan[25] and Hoffman, Armour, et al.[26,27] One-electron reduction of the complex $\mathrm{Ru(bpy)_2ClNO^{2+}}$ produced the six-coordinate $\mathrm{d^6}$ complex $\mathrm{Ru(bpy)_2ClNO^{+}}$ with reduction occurring at the nitrosyl group.[25] It should be noted that, in this complex, the ligand trans to the nitrosyl group is part of a bidentate bipyridine ligand, which would not be expected to be lost on reduction. $\mathrm{Ru(NH_3)_5NO^{3+}}$ has been reduced to $\mathrm{Ru(NH_3)_5NO^{2+}}$ by pulse radiolysis and electrochemical techniques in aqueous solution.[26] The resultant complex was unstable toward secondary reactions and reacted with the radical of *tert*-butyl alcohol to give an alkylnitroso complex.[27] The authors concluded that the reduction site was centered at the nitrosyl ligand, giving a complex describable as either $\mathrm{Ru^{II}}$–NO· or $\mathrm{Ru^{III}}$–NO.[26] A puzzling aspect of this problem, not addressed in our work, is the linear nitrosyl of $\mathrm{Fe(CN)_4NO^{2-}}$. Several models have been proposed to predict the geometry of the M–NO linkage as a function of electronic configuration.[28–30] These models, though differing in detail, predict a bent M–NO geometry for $\mathrm{Fe(CN)_4NO^{2-}}$, while the crystal structure shows an M–N–O angle of 177°.[18] Similarly, although the EPR spectra of the blue solutions have been interpreted as demonstrating the existence of a linear nitrosyl,[12,13] both the EPR and electronic spectra have been compared[9] to those obtained for the isoelectronic bis(dithiolato)iron(I) nitrosyls,[9,31] systems which have subsequently been shown to contain bent nitrosyls.[3]

The complex $\mathrm{Fe(CN)_4NO^{2-}}$ would thus seem to be an exception to the models which predict a bent M–NO geometry for $\mathrm{d^7}$ systems.

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Registry No. $\mathrm{Fe(CN)_5NO^{2-}}$, 15078-28-1; $\mathrm{Fe(CN)_4NO^{2-}}$, 51232-23-6; $\mathrm{Fe(CN)_4NO^{-}}$, 60706-14-1; $\mathrm{Fe(CN)_4NO^{3-}}$, 58904-86-2.

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