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On the Reactivity of Tetracyanonitrosylferrate(2–). III. Redox Reactivity of $[Fe(CN)_4NO]^{2-}$

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Abstract

Redox properties of the ion $[Fe(CN)_4NO]^{2-}$ were studied electrochemically both in non-aqueous and aqueous media in the absence of free cyanide ions. It was found that while the reduction proceeds smoothly the oxidation is not observed at the electrode in the attainable potential range, and can be achieved only by Br_2 oxidation taking place as oxidative addition. Aspects of the redox reactivity are discussed and the overall scheme of reactions of the tetracyanonitrosylferrate(2–) and derived species is given.

Introduction

The electrochemical studies of the species arising in the course of the reaction:

$$[Fe(CN)_5NO]^{2-} \xrightarrow[-CN]{1e^-} [Fe(CN)_4NO]^{2-} \xrightarrow[-CN]{\text{chel}} [Fe(chel)(CN)_3NO]^-$$

(chel = 2,2′-bipyridine or 1,10-phenanthroline) included in two previous parts of this series [1, 2] demonstrated that the redox behaviour of the metal–nitrosyl complexes reflected the distribution of the electron density between the metal and nitrosyl ligand: changes in the electron density distribution induced by alteration of the coordination sphere resulted in significant changes of the redox properties of the complex ion. Thus study of the redox reactivity of nitrosyl complexes can be very useful for the investigation of the nature of the metal–nitrosyl bond, which determines to a great extent the overall reactivity of the nitrosyl complex.

The published findings concerning the redox behaviour of the $[Fe(CN)_4NO]^{2-}$ anion [3–9] originated mostly from electrochemical studies of the nitroprusside ion $[Fe(CN)_5NO]^{2-}$ which, after one-electron reduction, can split off one cyanide ligand forming the anion $[Fe(CN)_4NO]^{2-}$ [8–13]. In these systems the presence of the free cyanide ions in addition to $[Fe(CN)_4NO]^{2-}$ results in coupled chemical equilibria which complicate the intrinsic electrochemical process and make it difficult to judge correctly the observed redox steps. The most complete scheme of the redox behaviour of the nitroprusside ion reduction products in aqueous medium is comprised in [8].

Bowden *et al.* [9] investigated the polarographic and voltammetric behaviour of the nitroprusside ion and its reduction products in organic aprotic solvents. On the basis of the finding of two anodic and one cathodic waves appearing in the reduced nitroprusside system, they proposed the redox scheme:

$$[Fe(CN)_4NO]^- \overset{-0.66\,V}{\rightleftharpoons} [Fe(CN)_4NO]^{2-} \overset{-1.23\,V}{\rightleftharpoons} [Fe(CN)_4NO]^{3-}$$

However there is reason to doubt the relevancy of the left-hand redox process because both oxidation waves appearing in the reduced nitroprusside system can be ascribed to a cyanide complex formation on the mercury electrode (see Results).

The existence of a second reduction step of tetracyanonitrosylferrate(2–) follows from the preparative study [12]:

$$[Fe(CN)_4NO]^{3-} \xrightarrow[-CN]{2e} [Fe(CN)_3NO]^{4-}$$

The reaction is considered to take place in liquid ammonia when using metallic sodium as the reducing agent.

In the present work we attempted to verify and to supplement the above mentioned conceptions concerning the redox properties of the $[Fe(CN)_4NO]^{2-}$ ion. To avoid any complications which can arise in consequence of the presence of free cyanide in solution, we used the pure salt tetrabutylammonium tetracyanonitrosylferrate(2–) as a starting material for all electrochemical experiments.

The tetraalkylammonium salt of $[Fe(CN)_4NO]^{2-}$ was originally prepared by Nast and Schmidt [12, 14] by the method based on the reduction of the nitroprusside ion by metallic sodium in liquid ammonia. We used for our purposes the more simple

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method, electrochemical reduction of tetrabutylammonium nitroprusside in acetonitrile.

Experimental

The arrangement for electrochemical experiments was described in [1].

Purification of Solvents

Acetonitrile, Fluka spectrograde, was refluxed over CaH_2 and freshly distilled. Dichloromethane was dried by storing with P_2O_5 and freshly distilled from P_2O_5. Diethylether was purified by passing through a column filled with activated alumina and stored over potassium hydroxide. Dimethylformamide was purified using sodium antracenide method [15]. Other chemicals used were of analytical grade.

Preparation of Tetrabutylammonium Tetracyanonitrosylferrate(2–)

A solution of 2×10^{-2} M tetrabutylammonium nitroprusside (prepared by metathesis from sodium nitroprusside and tetrabutylammonium bromide) and 10^{-1} M tetrabutylammonium perchlorate in acetonitrile was reduced electrochemically at the potential of the limiting current of the first nitroprusside wave using a large area mercury pool electrode as a working electrode and a carbon electrode in a separated anodic compartment as a counter electrode. The potential was controlled potentiostatically using a saturated calomel electrode (SCE) as a reference electrode. The blue, air-sensitive solution containing $[Fe(CN)_4NO]^{2-}$ was transferred to a Schlenk flask and diethylether was slowly added until blue crystals of tetrabutylammonium tetracyanonitrosylferrate(2) were formed. The crystalline product was dried several hours *in vacuo* at room temperature and was stored under argon.

Anal.: Calc. for $[(C_4H_9)_4]_2[Fe(CN)_4NO]$: C, 64.07; H, 10.75; N, 14.53. Found: C, 63.78; H, 10.71; N, 14.47%.

Preparation of Tetrabutylammonium Bromotetracyanonitrosylferrate(2–)

475 mg (1 mmol) of tetrabutylammonium tetracyanonitrosylferrate(2–) dissolved in 100 ml of deaerated dichloromethane was oxidized by adding the equivalent amount (25.6 μl) of bromine in a few milliliters of CH_2Cl_2. Dichloromethane was evaporated *in vacuo* and the remaining solid was recrystallized from acetonitrile/diethylether. The resulting yellow-green crystalline product was dried several hours *in vacuo* at room temperature and stored in inert atmosphere.

Anal. : Calc. for $[(C_4H_9)_4N]_2[FeBr(CN_4NO)]$: C, 57.29; H, 9.62; N, 12.99. Found: C, 57.18; H, 9.56; N, 13.25%.

The solutions of the $Na_2[Fe(CN)_4NO]$ and $Na_2[FeBr(CN)_4NO]$ for polarographic measurements in aqueous medium were prepared by dissolving sodium perchlorate (used in concentration 0.1 M as as supporting electrolyte) in an aqueous solution of the tetrabutylammonium salt. The precipitate of tetrabutylammonium perchlorate was filtered off.

Results

Electrochemistry of $[Fe(CN)_4NO]^{2-}$ in Nonaqueous Medium

Polarographic behaviour of the anion $[Fe(CN)_4NO]^{2-}$ in CH_2Cl_2 solution is demonstrated in Fig. 1.

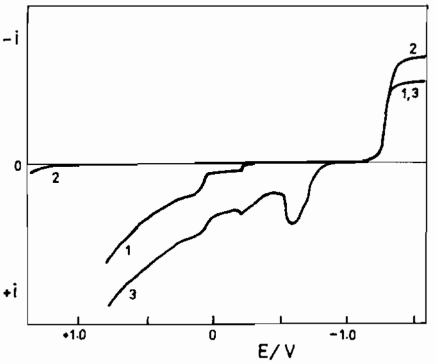


Fig. 1. Polarography of $[Bu_4N]_2[Fe(CN)_4NO]$ (10^{-3} M) in CH_2Cl_2, 0.1 M-$[Bu_4N]ClO_4$: (1) DME, (2) glassy carbon RDE, (3) DME on addition of 10^{-3} M-$[Bu_4N]CN$.

The reduction wave on the dropping mercury electrode (DME) (curve 1) corresponds to a one-electron, polarographically-reversible process ($\Delta E/\Delta \log((i_d - i)/i)$ = 60 mV) with the half-wave potential $E_{1/2}$ = −1.31 V *vs.* SCE (measured potentials corrected using bis(biphenyl)chromium iodide as a pilot ion). Cyclic voltammetry confirmed the reversibility of the reduction process and proved that no coupled chemical reaction is present which would influence the reversible shape of the cyclic voltammogram. No other reduction has been found, even at more negative potentials attainable in dimethylformamide.

The waves appearing on the anodic side of the polarogram using the DMF have non-diffusional character (checked by dependence $\log i_d - \log t_1$, found $\Delta \log i_d / \Delta \log t_1 \leqslant 0$ instead of 1/6 valid for diffusion controlled case) and they do not appear when the glassy carbon rotating disc electrode (RDE) is used (curve 2). Hence these waves are to be ascribed to a dissolution of mercury, promoted by formation of an adduct with the complex anion which is presumably adsorbed at the electrode.

Curve 3 in Fig. 1 shows the polarogram recorded on addition of tetrabutylammonium cyanide to the solution of tetrabutylammonium tetracyanonitrosyl-

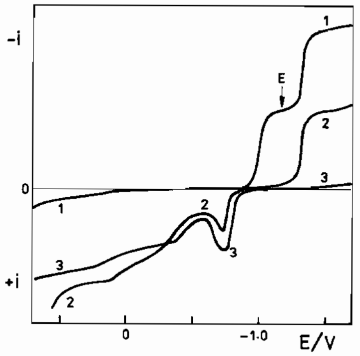


Fig. 2. Controlled potential electrolysis of $[Bu_4N]_2[Fe(CN)_5NO]$ on the mercury pool in CH_2Cl_2, 0.1 M-$[Bu_4N]ClO_4$: (1) 10^{-3} M-$[Bu_4N]_2[Fe(CN)_5NO]$ before electrolysis (2) on passing 1 *F*/mol at potential *E*, (3) 10^{-3} M-$[Bu_4N]CN$.

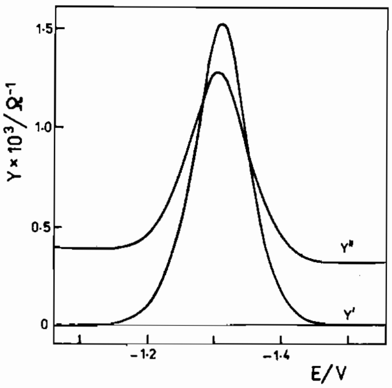


Fig. 3. A.C. phase-sensitive polarogram on DME of 10^{-3} M-$[Bu_4N]_2[Fe(CN)_4NO]$ in CH_3CN 0.1 M-$[Bu_4N]ClO_4$; f = 1020 Hz, $\Delta E_{a.c.}$ (top-to-top) = 15 mV. Y': in phase, Y'' quadrature component of electrode admittance.

ferrate(2–). The polarographic pattern is very close to that obtained by one-electron reduction of tetrabutylammonium nitroprusside in CH_2Cl_2 (Fig. 2, curve 2). Comparing this with the polarogram of tetrabutylammonium cyanide alone (curve 3 in Fig. 2) it is obvious that the anodic wave at about –0.7 V corresponds to free cyanide ions and not to the oxidation $Fe^{I} \rightarrow Fe^{II}$, as supposed until now [9].

The kinetics of the electrode reduction of the tetracyanonitrosylferrate(2–) was investigated using a.c. phase-sensitive polarography. Figure 3 shows an a.c. polarogram of the complex in acetonitrile. Results of the non-linear regression analysis using experimental values of the electrode admittance and fundamental theoretical relations valid for simple electrode reactions [16, 17]

$$Z'_F = (\xi + 1)R_{ct} \qquad \overleftarrow{k} = k_s\exp[-\alpha nF(E - E_o)RT]$$

$$Z''_F = \xi R_{ct} \qquad \overrightarrow{k} = k_s\exp[(1 - \alpha)nF(E - E_o)/\mathrm{RT}]$$

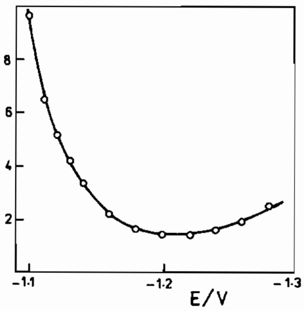


Fig. 4. Regression analysis of a.c. polarographic data from Fig. 3. (o) experimental values of $\xi = Y''_F\,(Y'_F - Y''_F)$, (——) regression curve corresponding to the parameters $k_s = 8.53 \times 10^{-2}$ cm s^{-1}, $\alpha = 0.2440$, $E_o = -1.300$ V *vs.* SCE.

$$\xi = \overrightarrow{k}/(2\omega\, D_R)^{1/2} + \overleftarrow{k}/(2\omega D_O)^{1/2}$$

are given in Fig. 4. Calculated parameters of the electrode process are: k_s (standard heterogeneous rate constant) = 8.5×10^{-2} cm s^{-1}, α (charge-transfer coefficient) = 0.244, E_o (standard redox potential) = –1.300 V.

Large area electrolysis of $[Bu_4N]_2[Fe(CN)_4NO]$ on mercury pool electrodes was performed in order to obtain the one-electron reduction product $[Fe(CN)_4NO]^{3-}$. In contrast to the reversibility of the reduction process observed with dropping mercury electrode, during the large area electrolysis only some electroactive decomposition products at different potentials were formed, irrespective of the solvent used (CH_2Cl_2, DMF, CH_3CN). Consequently, a relatively slow decomposition of $[Fe(CN)_4NO]^{3-}$ in used solvents must be supposed. Bowden *et al.* [9] came to the same results when performing the two-electron electrolysis of tetrabutylammonium nitroprusside.

Electrochemistry of [Fe(CN)$_4$NO]$^{2-}$ in Aqueous Medium

Nature of the electrode processes in water solution are essentially the same as in the aprotic media, *viz.*, a one-electron reversible reduction wave appears with the half wave potential $E_{1/2}$ = –0.58 V (*vs.* SCE). The electron consumption was confirmed by coulometry. Similarly, as in non-aqueous media, large area electrolysis proved the instability of the reduction product $[(Fe(CN)_4NO]^{3-}$ in solution. In contrast to the behaviour of the nitroprusside ion, no other more negative reduction wave has been found in the case of tetracyanonitrosylferrate. This confirms indirect evidence [6–8] about the relationship of the 'third nitroprusside wave' to the pentacyano species.

Formation and Properties of [Bu$_4$N]$_2$[FeBr(CN)$_4$NO]

As no oxidation of tetracyanonitrosylferrate(2–) on the electrode was found, we studied the interaction of the complex $[Bu_4N]_2[Fe(CN)_4NO]$ with bromine in order to examine the ability of tetracyanonitrosylferrate to be oxidized chemically. In a reaction proceeding as an oxidative addition, the yellow-green substance of the composition $[Bu_4N]_2[FeBr(CN)_4NO]$ was formed (see Experimental).

Polarographic behaviour of the ion $[FeBr(CN)_4NO]^{2-}$, which is isosteric with the nitroprusside anion $[Fe(CN)_5NO]^{2-}$, is shown in Fig. 5. As in the case of nitroprusside [9], the bromo-complex exhibits in the aprotic CH_2Cl_2 solution two reduction waves. The first reduction:

$$[FeBr(CN)_4NO]^{2-} \xrightarrow{1e} [FeBr(CN)_4NO]^{3-}$$

with the half-wave potential on the DME $E_{1/2} = -0.25$ V (irreversible, on the glassy carbon RDE shifted more negatively) was followed by a fast reaction in which the bromide ligand was split off and the resulting ion $[Fe(CN)_4NO]^{2-}$ was reduced in the second cathodic wave identical to that obtained for pure $[Fe(CN)_4NO]^{2-}$ salt ($E_{1/2} = -1.31$ V).

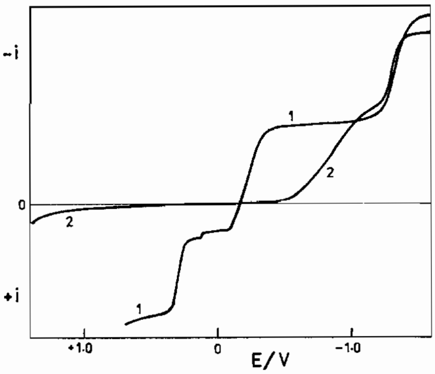


Fig. 5. Polarography of $[Bu_4N]_2[FeBr(CN)_4NO]$ (10^{-3} M) in CH_2Cl_2, 0.1 M-$[Bu_4N]ClO_4$: (1) DME, (2) glassy carbon RDE.

Anodic waves which appear close to the first cathodic wave (curve 1 in Fig. 5) were not observed when the mercury electrode was replaced by the glassy carbon electrode (curve 2); thus, they are caused by oxidation of mercury due to a formation of some adduct with the depolarizer. As no similar anodic waves were obtained with the nitroprusside ion, it can be assumed that the substitution of the cyanide ligand by the bromide ion probably results in a less stable complex from which the anionic ligands can be released by the interaction with mercury ions. The observed sensitivity of the bromo derivative to the exposition to air supports this presumption.

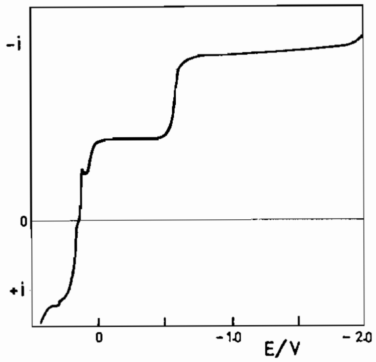


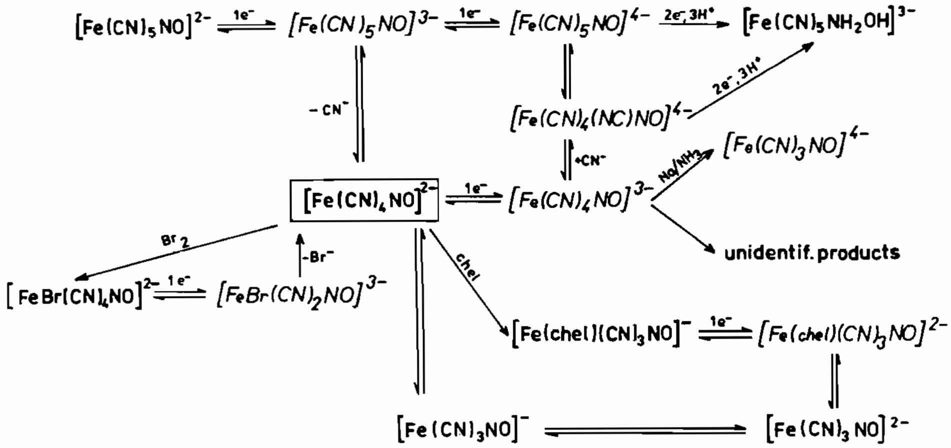
Fig. 6. Polarogram of 10^{-3} M-$Na_2[FeBr(CN)_4NO]$ in H_2O; 0.1 M $NaClO_4$.

The nature of the redox processes in water solution of $[FeBr(CN)_4NO]^{2-}$ is in principle the same as in aprotic media but the polarographic behaviour (Fig. 6) is complicated due to partial mixing of the anodic and cathodic currents.

Discussion

The results presented show that the only redox process pertinent to the ion $[Fe(CN)_4NO]^{2-}$ is the one-electron reduction. The reason why the d^7 (Fe^I) system involved in this ion does not undergo a simple oxidation may be that the HOMO orbital is sterically unattainable. Such an explanation is reasonable, because the HOMO (or SOMO = semi-occupied molecular orbital) a_1 is composed prevailingly of Fe-d_{z^2} orbital and σ_{NO} orbital (Mulliken populations 0.680 and 0.160 [11]) and is largely localized between iron and the nitrosyl ligand. Furthermore the X-ray analysis of $[Et_4N]_2[Fe(CN)_4NO]$ showed [10] that the metal atom is somewhat diverted towards the apex of the square pyramid, so that the cyanide ligands can partially screen the $d_{z^2}(a_1)$ orbital. Thus it appears that the pentacoordinate species can be oxidized only in the form of an oxidative addition as was shown in the reaction with bromine. On the other hand, if an appropriate ligand able to be bound in the sixth coordination site is present (as it is the case in the reoxidation of the reduced nitroprusside system), the oxidation can proceed due to the intramolecular electron transfer from iron to nitrosyl [1].

The resistance of the $[Fe(CN)_4NO]^{2-}$ ion towards electrode oxidation has the same behaviour as a similar d^7 pentacoordinate species, *viz.*, the $[Co(CN)_5]^{3-}$. This ion also is not oxidized at the electrode in aqueous media although it undergoes readily the oxidative addition. Similarly e.g. the



Scheme 1.

Vaska complexes of the type $IrX(CO)L_2$ can be oxidized electrochemically with great difficulty, whereas their oxidative additions proceed smoothly [18]. In all these cases the big difference in reactivity between the simple electrode oxidation and the redox addition can be explained by the fact that in addition to the stabilizing effect of coordination of additional ligand(s), the activation process concerns different orbitals of the original complex.

In contrast to the oxidation process, the reduction on the electrode proceeds with relatively low activation energy, as indicated by a.c. polarographic measurements. Consequently, the redox orbital is in this case probably not SOMO a_1 (d_{z^2}, σ_{NO}) but LUMO e_y ($\pi_y(NO)$, d_{yz}). The low value of the energy difference between the orbitals a_1 and e_y (7800 cm^{-1} calculated in [11]) also suggests that the reduced form $[Fe(CN)_4NO]^{3-}$ might be in the high spin $(a_1)^1$-$(e_y)^1$ = ^3E state. No further attempt to prove experimentally the above consideration was made, because of the instability of the anion $[Fe(CN)_4NO]^{3-}$ in solution.

The overall scheme of the reactions of tetracyanonitrosylferrate(2−) and derived species is presented in Scheme 1. Some of the depicted equilibria are strongly influenced by solvent and temperature. The species which are not stable in organic solvents at normal temperature are therefore written in italics.

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