ON THE ELECTROCHEMICAL, SPECTRAL AND PHOTOCHEMICAL PROPERTIES OF CYANO–NITROSYL COMPLEXES. A COMPARISON BETWEEN IRON AND RUTHENIUM ANALOGUES

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First order rate constant of cyanide splitting from one-electron product of the nitroprusside ion reduction was determined using a.c. polarography (k = 350 s^{-1} in CH_3CN). $[Ru(CN)_5(NO)]^{2-}$ ion is reduced reversibly ($E_{1/2}$ = −1.04 V, k^0 = 4.86 . 10^{-3} m s^{-1} in CH_3CN; $E_{1/2}$ = −0.39 V in H_2O) with one electron. IR and EPR study indicates dimerization of the reduction product in solution but no cyanide splitting from electrogenerated $[Ru(CN)_5(NO)]^{3-}$ was detected. Further reduction of $[Ru(CN)_5(NO)]^{3-}$, with consumption of protons, occurs in aqueous media. Efficient photochemical reactions of $[Fe(CN)_4(NO)]^{2-}$ with O_2, $KMnO_4$ and pyridine take place when the complex is excited at the metal-to-nitrosyl charge transfer band.

Extraordinary and, in many cases, confusing results obtained from various experimental conditions studying the path of nitroprusside ion reduction and the physico-chemical properties of its products have evoked an unusual number of studies on the subject (refs[1 – 5] and references therein). Only when the one-electron products were isolated and characterized[6 – 8], the properties of the reaction mixture, obtained by the reduction of the nitroprusside ion, could be clearly interpreted on the basis of the equilibrium existing in both aqueous and nonaqueous solutions.

$$[Fe(CN)_5(NO)]^{3-} \rightleftharpoons CN^- + [Fe(CN)_4(NO)]^{2-} \qquad (1)$$

A significant distinction in physical and chemical properties of the yellow (brown in solid) ion $[Fe(CN)_5(NO)]^{3-}$ and the blue species $[Fe(CN)_4(NO)]^{2-}$ is due to the different distribution of the electron density and the state of the coordinated nitrosyl ligand. $[Fe(CN)_5(NO)]^{3-}$ ion is assigned as $Fe^{II}–NO^0$ formal type, while $[Fe(CN)_4(NO)]^{2-}$ corresponds to the formulation $Fe^{I}–NO^+$ (refs[9,10]).

The equilibrium (*1*) is a case of intramolecular charge transfer between the metal and nitrosyl which involves change of the coordination number and symmetry. Such a type of reaction is generally denoted as "stereochemical control of valence" (ref.[11]) since the overall stereochemistry of the complex ion determines the formal oxidation state and consequently the geometry and chemical reactivity of the coordinated NO group.

The existence of reactions of this type, in which a significant change of redox, donor–acceptor and coordination properties takes place with a low energy barrier, provides a perspective for catalytic and synthetic chemistry. The ruthenium cyano–nitrosyl complexes have been much less investigated up to now, obviously due to difficulties with the preparation of sufficiently pure and soluble salts. Presented study of the reduction behaviour of $[Ru(CN)_5(NO)]^{2-}$ was evoked with the idea to check the behaviour of complexes which could follow analogous reaction scheme as reported for the iron species.

Photoexcitation at the wavelength of the charge-transfer band between the metal and the nitrosyl ligand provides an alternative method of achieving the change of the state and reactivity of M–NO moiety. This paper reports on the photochemical reactions of the $Fe^I–NO^+$ complex induced by excitation at the iron-to-nitrosyl charge transfer band.

EXPERIMENTAL

Chemicals

Tetrabutylammonium pentacyano-nitrosylferrate(2–), $(Bu_4N)_2[Fe(CN)_5(NO)]$, was prepared from sodium nitroprusside (analytical grade) by conversion with tetrabutylammonium bromide.

Tetrabutylammonium tetracyano-nitrosylferrate(2–), $(Bu_4N)_2[Fe(CN)_4(NO)]$, was electrosynthesized using the procedure described earlier[12].

A water soluble sodium salt of pentacyano-nitrosylruthenate(2–) was prepared using the method of nitrosation of the hot solution of a cyanocomplex ($Na_4[Ru(CN)_6]$ in this case) with gaseous NO/NO_2 (ref.[13]). To remove $NaNO_3$, $Na_4[Ru(CN)_5(NO_2)]$ and other side products, the evaporated crude product was extracted into ethanol/water mixture and crystallized repeatedly. For $Na_2[Ru(CN)_5(NO)]$. 2 H_2O (343.1) calculated: 17.50% C, 1.18% H, 24.50% N; found: 16.70% C, 1.08% H, 24.10% N. IR spectra (ν, cm^{-1}): 1 925 (NO), 2 070, 2 100 (CN).

Tetraphenylphosphonium pentacyano-nitrosylruthenate(2–), $(Ph_4P)_2[Ru(CN)_5(NO)]$, soluble in most polar organic solvents, was obtained by a conversion of the sodium salt with Ph_4PBr. For $[(C_6H_5)_4P]_2[Ru(CN)_5(NO)]$ (940.0) calculated: 67.74% C, 4.29% H, 8.95% N, 6.59% P; found: 66.42% C, 4.29% H, 8.99% N, 6.46% P. IR spectra (ν, cm^{-1}): 1 870 (NO), 2 060, 2 110 (CN).

Acetonitrile for electrochemical purposes was pre-dried over a molecular sieve. It was then dried with phosphorus pentoxide and distilled with a small amount of P_2O_5. The distillate was refluxed for several hours with calcium hydride under an argon atmosphere and fractionally distilled.

Trideuterioacetonitrile (Merck) was used for simultaneous electrochemical and IR measurements.

Dichloromethane was dried repeatedly with fresh portions of phosphorus pentoxide, decanted and distilled from P_2O_5 and afterwards refluxed with lithium aluminum hydride under an inert atmosphere. The amount of the solvent required for an experiment was freshly distilled from $Li[AlH_4]$.

Commercial argon was passed under pressure 0.5 MPa through a column filled with a molecular sieve and cooled to –80 °C in order to remove any traces of moisture.

Air sensituve solutions (reduced complexes) were handled either under argon atmosphere in a Schlenk type glassware[14] or using the vacuum line technique.

Electrochemical Apparatus

Electrochemical experiments were performed using the multipurpose electrochemical instrument GWP 673 (Germany). A Tektronix 5103N oscilloscope supplemented with 5D10 Waveform Digitizer was employed as a recording device for fast-scan voltammetry.

An aqueous saturated calomel electrode (SCE) was used as a reference electrode in all electrochemical experiments. Measured nonaqueous solutions were separated from the aqueous reference electrode system by an electrolyte bridge containing corresponding supporting electrolyte (0.1 M tetrabutylammonium perchlorate in the nonaqueous solvent). Potentials in non-aqueous solutions were corrected using the pilot substance bis(biphenyl)chromium iodide. The value −0.816 V (ref.[15]) was considered as the standard potential $E^0(\mathrm{BBCrI}/\mathrm{BBCrI}^-)$ related vs SCE.

Spectra

UV VIS spectra were measured using an HP8452A diode array spectrometer. Luminiscence spectra were measured with Perkin–Elmer LS5B spectrometer. IR spectra (in KBr) were measured with Philips PU 9800 FTIR spectrometer. EPR measurements were performed with a Varian E-4 spectrometer using either a normal cell or a cell adapted for in situ electrolysis.

Spectroelectrochemistry

Two alternative methods were used for spectral measurements of in situ reduced species:

1. Optical transparent thin layer electrochemistry (OTTLE). A cell developed for measurements in a very inert atmosphere[16] had a cell thickness of 0.1 mm. A gold minigrid was used as a working electrode.

2. A parallel electrochemical and spectral measurement in a special spectroelectrochemical cell comprised of a 10 mm couvette sealed to the electrochemical vessel. The arrangement enables simultaneous registration of spectra and polarographic curves (on a dropping mercury electrode) during a large scale electrolysis on a mercury pool electrode. A sufficient homogenization of the solution in the cell was established by magnetic stirring. A Unicam SP 800 UV VIS spectrometer was adapted for the use of this cell.

Photochemical Experiments

Samples were irradiated in a 10 mm spectral cell with a 500 W lamp equiped with a monochromator.

Evaluation of Kinetic Parameters from A. C. Polarographic Data for a Simple Electrode Reaction

Theoretical expressions for the faradaic impedance in the case of a simple electrode process[17]

$$Z_F' = (\zeta + 1) R_{ct}, \qquad Z_F'' = \zeta R_{ct}, \qquad \zeta = \overrightarrow{k}/(2\omega D_R)^{1/2} + \overleftarrow{k}/(2\omega D_O)^{1/2},$$

$$\overleftarrow{k} = k^0 \exp[-\alpha n F (E - E^0)/R T], \qquad \overrightarrow{k} = k^0 \exp[(1-\alpha) n F (E - E^0)/R T],$$

were rearranged to give a suitable regression function

$$y = a \exp(-\alpha x) + b \exp[(1 - \alpha) x],$$

where

$$y = \zeta = Z_F''/(Z_F' - Z_F'') = Y_F''/(Y_F' - Y_F''), \qquad x = n F E/R T$$

and parameters

$$a = k^0 (2\,\omega D)^{-1/2} \exp\,[\alpha\, n F E^0/R T]\,, \qquad b = k^0 (2\,\omega D)^{-1/2} \exp\,[(\alpha - 1)\, n F E^0/R T]\,.$$

Once the parameters a, b are evaluated from the analysis of the experimental dependence of the components of electrode admittance (Y', Y'') on potential, the standard heterogeneous rate constant of the electrode reaction and the standard redox potential is explicitly expressed:

$$k^0 = (2\,\omega D)^{1/2}\, a^{(1-\alpha)}\, b\,, \qquad E^0 = (R T/n F) \ln (a/b)\,.$$

Evaluation of Kinetic Parameters from A. C. Polarographic Data for a Reversible Electrode Reaction with Rapid Inactivation

The expression for the phase angle between the components of faradaic impedance follows from Smith's[18] general solution of the mechanism:

$$\mathrm{O} + n\,\mathrm{e} \overset{k_0}{\rightleftharpoons} \mathrm{R} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \mathrm{Y}$$

$$\operatorname{cotg} \varphi = Y_F'/Y_F'' = V/S$$

$$V = \frac{(2\,\omega)^{1/2}}{\lambda} + \frac{1}{1+e^j}\left\{1 + \frac{K e^j}{1+K} + \frac{e^j}{1+K}\left[\frac{(1+k^2/\omega^2)^{1/2} + k/\omega}{1+k^2/\omega^2}\right]^{1/2}\right\}$$

$$S = \frac{1}{1+e^j}\left\{1 + \frac{K e^j}{1+K} + \frac{e^j}{1+K}\left[\frac{(1+k^2/\omega^2)^{1/2} - k/\omega}{1+k^2/\omega^2}\right]^{1/2}\right\}$$

$$\lambda = \frac{k^0}{D^{1/2}} (e^{-\alpha j} + e^{(1-\alpha) j}) \qquad j = \frac{n F}{R T}(E - E^0)$$

$$K = k_1/k_2 \qquad k = k_1 + k_2\,.$$

Introducing the conditions of reversibility of the electrode process ($\omega/\lambda^2 \to 0$) and irreversibility of the coupled chemical reaction ($k_2 >> k_1$, $k \approx k_2$, $K \approx 0$) the function available for a regression analysis is obtained after some rearrangements:

$$y = (1 + a\, e^x)/(1 + b\, e^x)$$

$$y = \mathrm{cotg}\,\varphi = Y_F'/Y_F'' , \qquad x = nFE/RT .$$

Parameters a and b stand for:

$$a = \left[\frac{(1 + k^2/\omega^2)^{1/2} + k/\omega}{1 + k^2/\omega^2}\right]^{1/2} \exp\left[\frac{-nF}{RT} E^0\right]$$

$$b = \left[\frac{(1 + k^2/\omega^2)^{1/2} - k/\omega}{1 + k^2/\omega^2}\right]^{1/2} \exp\left[\frac{-nF}{RT} E^0\right] .$$

When the parameters a and b are obtained from the regression analysis of experimental data, the standard redox potential and the rate constant of the consecutive chemical reaction is expressed explicitly:

$$E^0 = (RT/nF) \ln [2\, a^{1/2} b^{1/2}/(a^2 + b^2)] , \qquad k = (\omega/2)\,(a/b - b/a) .$$

RESULTS AND DISCUSSION

Iron Complexes

Electrochemical and spectral properties of the ions $[Fe(CN)_5(NO)]^{2-}$, $[Fe(CN)_5(NO)]^{3-}$ and $[Fe(CN)_4(NO)]^{2-}$ were mostly described earlier[1 - 4,9,12,19]. In the present work additional a.c. polarographic and photochemical experiments were carried out.

A.c. polarography was used for the quantitation of the mobility of equilibrium (*1*) in a nonaqueous medium. A.c. phase sensitive polarographic data registered at potentials of the one-electron reduction of $(Bu_4N)_2[Fe(CN)_5(NO)]$ in an acetonitrile solution were treated using the mathematical relations valid for the scheme of reversible reduction with inactivation of the product (see Experimental). This simplification of the general electrode reaction scheme is reasonable for the measurement at low a.c. frequences, as d.c. polarography has indicated a reversible electrode reaction (60 mV slope in E vs $\log[(i_d - i)/i]$ plot and, under the same conditions, a cyclic voltammetry experiment (up to 100 V s^{-1}) has shown no reverse anodic peak (the dissociation equilibrium (*1*) is fast and is shifted entirely to the side of products). The result of processing of the a.c. polarographic data obtained at the frequency 10 Hz is given in Fig. 1. The value of the rate constant of the dissociation of CN^- from $[Fe(CN)_5(NO)]^{3-}$ in acetonitrile, $k = 350 \pm 15\ s^{-1}$, is of the same order as has been found in an aqueous medium (280 s^{-1}, ref.[19]). (It should be mentioned that free cyanide ions, if present in aqueous solutions, shift the equilibrium (*1*) considerably to the left side[3].)

The surprising resistance of Fe^{I}–NO^{+} ion, $[Fe(CN)_4(NO)]^{2-}$, to oxidation[23] was reinvestigated under conditions of photoexcitation at the wavelength of the metal to nitrosyl charge transfer band (620 nm). The idea was that a photoinduced change of the type (from Fe^{I}–NO^{+} to Fe^{II}–NO^{0}) could lead to a species with sufficiently long lifetime and the redox properties analogous to those of $[Fe(CN)_5(NO)]^{3-}$ which is easily oxidable.

Indeed, $(Bu_4N)_2[Fe(CN)_4(NO)]$ undergoes a photochemical reaction with oxidation agents $KMnO_4$, O_2 (Fig. 2 shows UV VIS spectra in the course of a typical experiment), though an irradiation of a deaerated solution of the complex in organic solvents has no effect. Voltammetric monitoring of the products of the photooxidation (Fig. 3) indicates that the primary oxidation product (peak A) is not stable and is converted consecutively into the secondary product (peak B). Polarographic and spectral analysis of the solution resulting from the reaction detected a mixture of products; the nitroprusside ion, $[Fe(CN)_5(NO)]^{2-}$ was found to be the only species in which the metal–nitrosyl structure is saved.

Experiments focused on the verification of the ability of the pentacoordinated ion $[Fe(CN)_4(NO)]^{2-}$ to accept a sixth ligand when photochemically transferred into the Fr^{II}–NO^{0} type, have shown that strong aromatic immine bases can react with the photoexcited $[Fe(CN)_4(NO)]^{2-}$ ion. Visible spectra registered during the photochemical conversion of pyridine solution of blue tetrabutylammonium tetracyano-nitro-

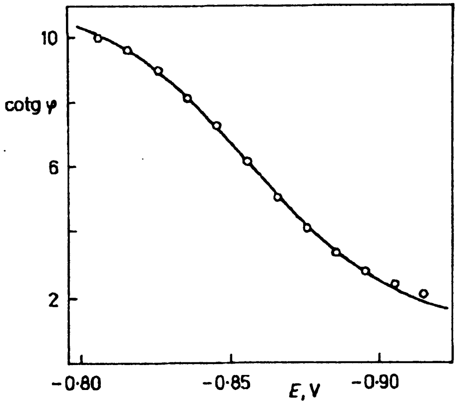

FIG. 1

Regression analysis of a.c. polarographic data. 10^{-3} M $(Bu_4N)_2[Fe(CN)_5(NO)]$ in CH_3CN/0.1 M Bu_4NClO_4; f = 10 Hz, $E_{a.c.}$ (peak-to-peak) = 15 mV, (Y') in phase, (Y'') quadrature component of electrode admittance: ○ experimental values of Y_F'/Y_F'', —— regression curve corresponding to the parameters $k = 350\ s^{-1}$, $E^0 = -0.917$ V (vs SCE)

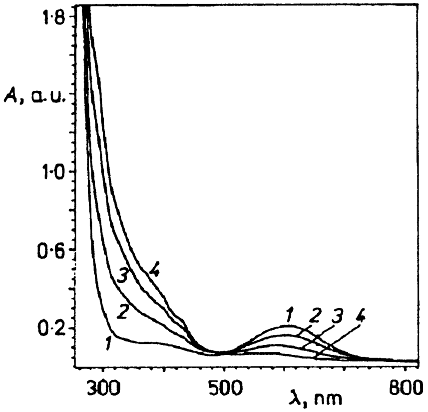

FIG. 2

Absorption spectra in course of photochemical reaction of tetracyano-nitrosylferrate with oxygen: *1* 5 . 10^{-4} M $(Bu_4N)_2[Fe(CN)_4(NO)]/CH_3CN$ saturated with O_2, *2* – *4* irradiation (620 nm) 3, 5, and 20 min, respectively sylferrate(2–) into the red coloured adduct are given in Fig. 4. The reaction product can be reversibly oxidized at the potential –0.1 V (polarographic $E_{1/2}$ vs SCE in pyridine solution) which supports the formulation of the species as the NO^0-type, with an oxidable nitrosyl ligand. EPR measurements indicate that the photochemically formed complex is probably dimerized, as follows from the observation that the EPR signal of the $[Fe(CN)_4(NO)]^{2-}$ ion diminishes during the photoreaction and no new signal appears, neither at room temperature nor at 77 K. A further characterization of the species is plagued by its instability: any attempt to isolate the product from the pyridine solution resulted in decomposition.

The photoreaction of $[Fe(CN)_4(NO)]^{2-}$ with methyl-substituted pyridine (2-methylpyridine) is much slower and no reaction was detected with pyridine substituted with the electronegative halogen (2-chloropyridine). Hence, it follows that maximal electron density on aromatic nitrogen is needed for efficient reaction.

Although the effective photochemical reactions of tetracyano-nitrosylferrate(2–) indicate the existence of a long-lived excited state, the deexcitation is completely nonradiative. No emission was found even when the luminiscence measurement was performed at the temperature of liquid nitrogen.

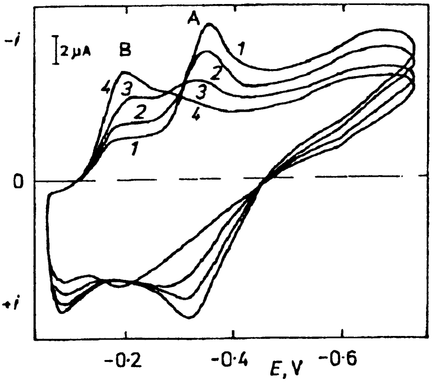

FIG. 3

Decay of the primary product of the photochemical reaction of tetracyano-nitrosylferrate with oxygen, voltammograms 0.5 Vs^{-1}: *1* 5 . 10^{-4} M $(Bu_4N)_2[Fe(CN)_4(NO)]$ saturated with O_2 and irradiated with projector lamp (100 W) 20 s, *2* – *4* time dependence in darkness; time interval between voltammograms is 5 s

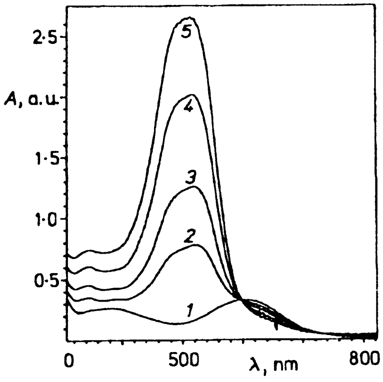

FIG. 4

Absorption spectra in course of photochemical reaction of tetracyano-nitrosylferrate with pyridine: *1* 8 . 10^{-4} M $(Bu_4N)_2[Fe(CN)_4(NO)]$ in pyridine, *2* – *5* irradiation (620 nm) 1, 5, 20, and 40 min, respectively

Ruthenium Complexes

Absorption spectra of synthesized salts, $Na_2[Ru(CN)_5(NO)]$ and $(Ph_4P)_2[Ru(CN)_5(NO)]$, are presented in Fig. 5. The absorption spectra in water (sodium salt) and in acetonitrile (tetraphenylphosphonium salt) are practically identical (with the exception of intense absorption bands of the cation Ph_4P^+ in UV region). hence, the inconsistencies in the published spectra (cf. ref.[20]) are not caused by differences in cation or medium used, but probably by the presence of an impurity in various preparations (a crude product usually contains $Na_4[Ru(CN)_6]$, $Na_4[Ru(CN)_5(NO_2)]$).

Both salts of pentacyano-nitrosylruthenate(2−) exhibit a weak emission (λ_{max} = 325 nm for $Na_2[Ru(CN)_5(NO)]$ in H_2O, λ_{max} = 335 nm for $(Ph_4P)_2[Ru(CN)_5(NO)]$ in acetonitrile) when excited in the near UV region (λ_{exc} = 290 nm). Surprisingly, we did not detect any emission of the solution resulting from electroreduction of $(Ph_4P)_2[Ru(CN)_5(NO)]$.

The polarogram of $Na_2[Ru(CN)_5(NO)]$ in water solution is shown in Fig. 6. The first reduction wave ($E_{1/2}$ = −0.39 V) is one-electron and reversible. The second one ($E_{1/2}$ =

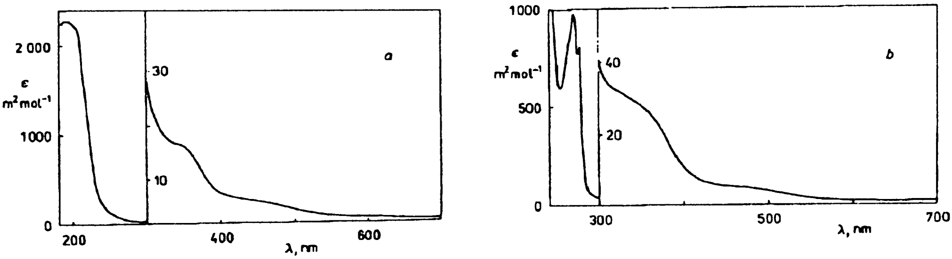

FIG. 5

Absorption spectra of pentacyano-nitrosylruthenate(2−): *a* sodium salt in water solution, *b* tetraphenylphosphonium salt in acetonitrile

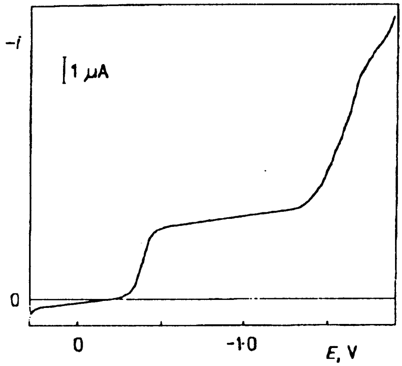

FIG. 6

Polarogram of 10^{-3} M $Na_2[Ru(CN)_5(NO)]$ in $H_2O/0.1$ M $NaClO_4$

−1.60 V) is irreversible. A large scale electrolysis at the potential of the second wave gives rise (in unbuffered solution) to an anodic polarographic wave of OH^- ions which confirms a consumption of protons during the reduction. The number of electrons needed for the total reduction could not been exactly determined (coulometrically), because the one-electron reduction product is not stable in water solutions. With respect to the ratio of the limiting currents of the polarographic waves, it can be assumed that the second wave corresponds to the reduction of NO to NH_2OH, analogously to the case of the isoelectronic iron complex[3].

In non-aqueous media, one-electron reversible reduction ($E_{1/2}$ = −1.04 V in acetonitrile) is the only electrode process found (except for the more negative cathodic wave due to the cation tetraphenylphosphonium). Figure 7 shows polarographic and spectrometric recordings during large scale electrolysis in the spectroelectrochemical cell. Figure 8 shows the spectra collected in the course of the OTTLE experiment. The new absorption bands (λ_{max} = 355 nm, shoulder 300 nm), arised upon the one-electron reduction of nitrosyl (Figs 7*a*, 8*a*), diminishes when the reduced complex is reoxidized electrochemically, and the original spectrum of $[Fe(CN)_5(NO)]^{2-}$ is restored at the end of the experiment (Fig. 8*b*). Also the polarographic curves show (Fig. 7) that the reduction of $[Ru(CN)_5(NO)]^{2-}$ is completely reversible (electrochemically and chemically) without any indication of the cyanide ligand splitting off. (Free cyanide ions would have been detected by an anodic wave at −0.7 V.)

The standard heterogeneous rate constant of the electrode reaction was determined from a.c. polarographic measurements in acetonitrile. The experimental values of the electrode admittance were analysed (for procedure see Experimental) and using the diffusion coefficient $D = 5.85 \cdot 10^{-10}$ m^2 s^{-1} (determined from the comparison of pola-

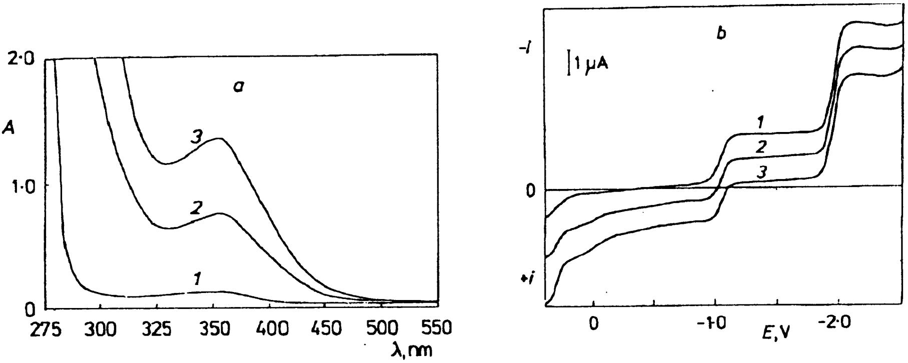

FIG. 7

Spectrophotometric (*a*) and polarographic (*b*) monitoring of the electrolysis in 10 mm spectroelectrochemical cell: *1* 7 . 10^{-4} M $(Ph_4P)_2[Ru(CN)_5(NO)]$ in CH_3CN/0.1 M $BuNClO_4$, *2* on passing 0.5 F mol^{-1} at −1.1 V, *3* on passing 1.0 F mol^{-1}

rographic limiting currents of the ruthenium complex and the pilot ion, ferrocene[21]) provided the result $k^0 = (4.86 \pm 0.15) \,.\, 10^{-3}$ m s^{-1} (Fig. 9).

Attempts to find the NO stretching frequency in the IR spectrum of $[Ru(CN)_5(NO)]^{3-}$ solution have been not successful. The possible explanation of this puzzle fact is formation of a dimer in which both nitrogen and oxygen atoms are involved in the bridged bond.

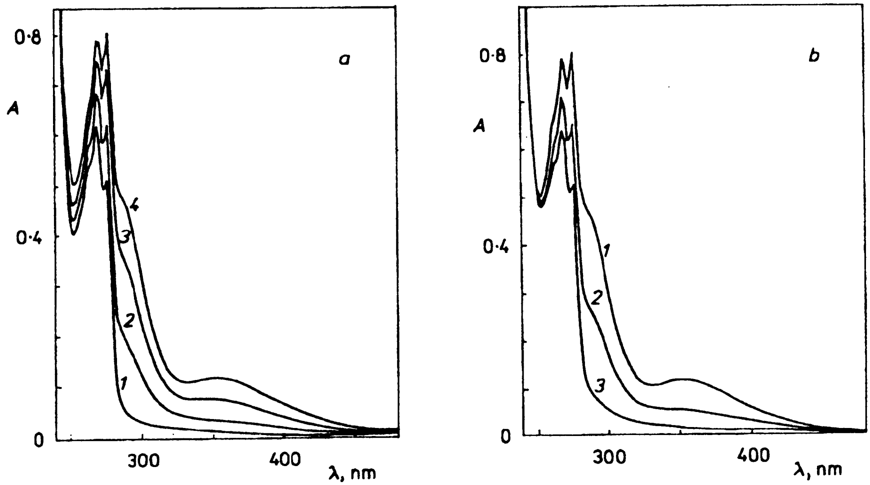

FIG. 8

OTTLE experiment. *a*: *1* UV VIS spectrum of $5 \,.\, 10^{-3}$ M $(Ph_4P)_2[Ru(CN)_5(NO)]$ in $CH_3CN/0.1$ M Bu_4NClO_4, *2* – *4* spectra recorded during reduction at −1.2 V; *b*: *1* reduced solution, *2* – *4* reoxidation at −0.5 V

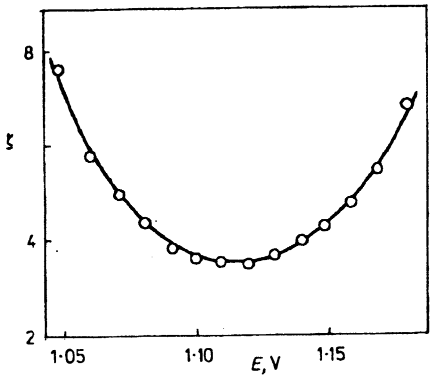

FIG. 9

Regression analysis of a.c. polarographic data. 10^{-3} M $(Ph_4P)_2[Ru(CN)_5(NO)]$ in $CH_3CN/0.1$ M Bu_4NClO_4; $f = 1\,020$ Hz, $E_{a.c.}$ (peak to peak) = 15 mV; ○ experimental values $\zeta = Y_F''/(Y_F' - Y_F'')$, —— regression curve corresponding to the parameters $k^0 = 4.86 \,.\, 10^{-3}$ m s^{-1}, $\alpha = 0.41$, $E^0 = -1.047$

EPR spectra measurements of the ion $[Ru(CN)_5(NO)]^{3-}$, generated electrochemically from $(Ph_4P)_2[Ru(CN)_5(NO)]$ in acetonitrile, have shown a weak triplet with $g = 2.027$ and $a_N = 1.50$ T (splitting with $^{14}N(I = 1)$). The low intensity of the signal which corresponds to only approx. 2% of expected concentration of unpaired electrons (no occurance of EPR signal at all is claimed in ref.[13]), supports the hypothesis of a dimer formation as follows from the IR spectra measurement. The dimerization mechanism is not in a contradiction with the above claimed electrochemical and chemical reversibility of the $[Ru(CN)_5(NO)]^{2-}/[Ru(CN)_5(NO)]^{3-}$ system, supposing that the dimerization reaction is reversible and sufficiently mobile. In addition, the anodic wave obtained after the one-electron reduction of $(Ph_4P)_2[Ru(CN)_5(NO)]$ was found to be decreased to approx. 75% in comparison with the original cathodic polarographic wave (Fig. 7). This decrease could be caused by the limited rate of the reverse reaction in the dimerization equilibrium and/or by the lower diffusion coefficient of the dimer.

CONCLUSIONS

Redox properties of the isoelectronic (d^6) species $[Fe(CN)_5(NO)]^{2-}$ and $[Ru(CN)_5(NO)]^{2-}$ are basically identical. The one-electron reduction related to the presence of the NO^+ redox centre yields initially the $[M(CN)_5(NO)]^{3-}$ species which can be reversibly oxidized and, in the presence of protons, undergo reduction of NO to NH_2OH. (Potentials are summarized in Table I.) However, the chemical behaviour of the relatively unstable one-electron reduction product is different. The ion $[Fe(CN)_5(NO)]^{3-}$ undergoes intramolecular (nitrosyl-to-iron) electron transfer which is connected with the elimination of a cyanide ligand and formation of tetracyano–nitrosyl complex. $[Fe(CN)_4(NO)]^{2-}$ ion is electrochemically reduced in a subsequent step. This mechanism makes it difficult to follow the further electrochemical activity of the original hexacoordinated species and its reduction potential was deduced only from the mechanism of reduction of the nitroprusside ion in aqueous solution[3].

TABLE I
Reduction potentials

Complex	$E_{1/2}$ vs SCE ,V	
	water	acetonitrile
$[Fe(CN)_5(NO)]^{2-}$	-0.33^a	-0.81
$[Ru(CN)_5(NO)]^{2-}$	-0.39	-1.04
$[Fe(CN)_5(NO)]^{3-}$	-1.46^a	–
$[Ru(CN)_5(NO)]^{3-}$	-1.60	–
$[Fe(CN)_4(NO)]^{2-}$	-0.58^b	-1.30^b

[a] Ref.[3]; [b] ref.[23].

In the case of ruthenium, no second redox step was found to follow the reversible one-electron reduction of $[Ru(CN)_5(NO)]^{2-}$ in aprotic media. This result suggests that no reaction involving electron transfer from nitrosyl to ruthenium occurs. The odd electron in $[Ru(CN)_5(NO)]^{2-}$ remains predominantly localized on the nitrosyl ligand and as follows from spectral (IR and EPR) findings, a stabilization of primarily formed ion takes place most probably via a dimer formation. However, reduction with a second electron occurs when cyanides are substitued with ligands of higher π-acceptor ability, e.g. 2,2′-bipyridine (cf. electrochemical reduction of $[Fe(bpy)(CN)_3(NO)]^-$ and $[Ru(bpy)_2(NO)Cl]^+$ in refs[22,23]).

The comparison of the spectral characteristics of reduced forms of the pentacyano-nitrosyl complexes is given in Table II. The odd electron in the $e(\pi^*_{NO})$ orbital of the one-electron product of the reduction of $[M(CN)_5(NO)]^{2-}$ gives rise to two allowed bands in the electronic spectrum, $^2E \rightarrow {}^2B_1$ and $^2E \rightarrow {}^2A_1$, corresponding to the charge transfers from nitrosyl to metal *d*-orbitals ($(e(\pi^*_{NO}) \rightarrow b_1\ (x^2 - y^2)$ and $(e(\pi^*_{NO}) \rightarrow a_1\ (z^2)$, cf. MO diagram in ref.[24]). Experimental maxima can be simply assigned to the predicted transfers in the case of the iron complex but for the ruthenium species the situation is complicated by the presumed presence of the dimerization equilibrium in solution. The complete characterization of the Ru species formed on the reduction of $[Ru(CN)_5(NO)]^{2-}$ will require to develop a convenient method for isolation of the low-valent ruthenium complex in solid state.

Photoinduced transfer $Fe^I{-}NO^+ \rightarrow Fe^{II}{-}NO^0$ give arise to the considerable photochemical activity of coordinatively unsaturated tetracyano-nitrosylferrate(2–). Detailed characterization of the photoreactions and their products is difficult for the instability of the species formed. In contrary to expectations, formation of the pentacoordinated species does not take place in the case of the ruthenium analogue but a stabilization of the unpaired electron by a dimerization of $[Ru(CN)_5(NO)]^{3-}$ is preferred. Hence, the study of the photochemical reactions connected with metal-to-nitrosyl charge transfer

TABLE II
CT maxima in electronic spectrum of reduced complexes

$[Fe(CN)_5(NO)]^{3-}$ [a]		Assignment	$[Ru(CN)_5(NO)]^{3-}$ [b]	
λ_{max} nm	ε $m^2\ mol^{-1}$		λ_{max} nm	ε $m^2\ mol^{-1}$
345	350	$^2E \rightarrow {}^2A_1$	300[c]	1 000
430	55	$^2E \rightarrow {}^2B_1$	355	215

[a] In water, values from ref.[19]; [b] in acetonitrile, this work; [c] shoulder.

could not be extended to more lucrative (from the photochemical point of view) ruthenium. Searching for other more convenient ruthenium analogues is in progress.

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REFERENCES

1. Kolthoff I. M., Torren P. E.: J. Am. Chem. Soc. *75*, 1197 (1953).
2. Van Woorst J. D. W., Hammerich P.: J. Chem. Phys. *45*, 3914 (1966).
3. Mašek J., Mášlová E.: Collect. Czech. Chem. Commun. *39*, 2141 (1974).
4. Bowden W. E., Bonnar P., Brown D. B., Geiger W. E. jr.: Inorg. Chem. *16*, 41 (1977).
5. Butler A. R., Glidewell Ch.: Chem. Soc. Rev. *16*, 361 (1987).
6. Nast R., Schmidt J.: Angew. Chem. *81*, 399 (1969).
7. Nast R., Schmidt J.: Z. Anorg. Allg. Chem. *421*, 15 (1976).
8. Dorn W. L., Schmidt J.: Inorg. Chim. Acta *16*, 223 (1976).
9. Schmidt J., Kuhr H., Dorn W. L., Kopf J.: Inorg. Nucl. Chem. Lett. *10*, 55 (1974).
10. Fiedler J., Mašek J.: Inorg. Chim. Acta *81*, 117 (1984).
11. Enemark J. H., Feltham R. D.: Coord. Chem. Rev. *13*, 339 (1974).
12. Fiedler J., Mašek J.: Inorg. Chim. Acta *111*, 39 (1986).
13. Durig J. R., McAllister W. A., Willis J. N. jr., Merler E. E.: Spectrochim. Acta *22*, 1091 (1966).
14. Herzog S., Dehnert J.: Z. Chem. *4*, 1 (1964).
15. Gritzner G.: Inorg. Chim. Acta *24*, 5 (1977); Diggle J. W., Parker A. J.: Electrochim. Acta *18*, 975 (1973).
16. Krejčík M.: *Ph.D. Thesis*. The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Academy of Sciences of the Czech Republic, Prague 1991.
17. Smith D. E. in: *Electroanalytical Chemistry* (A. J. Bard, Ed.), Vol. 1, Chap. 1, p. 26. Dekker, New York 1964; De Levie R., Pospíšil L.: J. Electroanal. Chem. *22*, 277 (1975).
18. Smith D. E. in: *Electroanalytical Chemistry* (A. J. Bard, Ed.), Vol. 1, Chap. 1, p. 40. Dekker, New York 1964.
19. Cheney R. P., Simic M. G., Hoffman M. Z., Taub I. A., Asmus K. D.: Inorg. Chem. *16*, 2187 (1977).
20. Butler A. R., Calsy-Harrison A. M., Glidewell Ch., Johnson I. L.: Inorg. Chim. Acta *146*, 187 (1988).
21. Kadish K. M., Ding J. Q., Malinski T.: Anal. Chem. *56*, 1741 (1984).
22. Callahan R. W., Brown G. M., Meyer T. J.: J. Am. Chem. Soc. *97*, 894 (1975).
23. Fiedler J., Mašek J.: Inorg. Chim. Acta *105*, 83 (1985).
24. Manoharan P. T., Gray H. B.: J. Am. Chem. Soc. *87*, 3340 (1965).

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