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Kinetics and Mechanism of the Formation of Nitroprusside from Aquapentacyanoferrate(III) and NO: Complex Formation Controlled by Outer-Sphere Electron Transfer

Federico Roncaroli,[†,‡] José A. Olabe,*[,‡] and Rudi van Eldik*[,†]

Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1,
91058 Erlangen, Germany, and Department of Inorganic, Analytical and Physical Chemistry,
Inquimae, Faculty of Exact and Natural Sciences, University of Buenos Aires,
C1428EHA Buenos Aires, Argentina

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The kinetics and mechanism of the reaction between nitric oxide and aquapentacyanoferrate(III) were studied in detail. Pentacyanonitrosylferrate (nitroprusside, NP) was produced quantitatively in a pseudo-first-order process. The complex-formation rate constant was found to be 0.252 ± 0.004 M^{-1} s^{-1} at 25.5 °C, pH 3.0 ($HClO_4$), and $I = 0.1$ M ($NaClO_4$), for which the activation parameters are $\Delta H^‡ = 52 \pm 1$ kJ mol^{-1}, $\Delta S^‡ = –82 \pm 4$ J K^{-1} mol^{-1}, and $\Delta V^‡ = –13.9 + 0.5$ cm^3 mol^{-1}. These data disagree with earlier studies on complex-formation reactions of aquapentacyanoferrate(III), for which a dissociative interchange (I_d) mechanism was suggested. The aquapentacyanoferrate(II) ion was detected as a reactive intermediate in the reaction of aquapentacyanoferrate(III) with NO, by using pyrazine and thiocyanate as scavengers for this intermediate. In addition, the reactions of other $[Fe^{III}(CN)_5L]^{n-}$ complexes ($L = NCS^-$, py, NO_2^-, and CN^-) with NO were studied. These experiments also pointed to the formation of Fe(II) species as intermediates. It is proposed that aquapentacyanoferrate(III) is reduced by NO to the corresponding Fe(II) complex through a rate-determining outer-sphere electron-transfer reaction controlling the overall processes. The Fe(II) complex rapidly reacts with nitrite producing $[Fe^{II}(CN)_5NO_2]^{4-}$, followed by the fast and irreversible conversion to NP.

Introduction

The reaction between nitric oxide and metal complexes has biochemical and environmental relevance.[1−3] Nitric oxide has been shown to play an important role in mammalian biology, including cytotoxic immune response, intracellular signaling,[1−7] and blood pressure regulation.[8] In addition, processes that have to do with the transport and storage of NO involve reactions with metal centers, as typically found in coordination chemistry. Among others, iron complexes have been recognized as useful models for biological systems and have been used to investigate specific binding sites in amino acids and redox reactions of metalloproteins.[9]

Studies on the coordination of NO to transition metal centers are rather scarce.[1−3] Fundamental questions arise as to the free radical nature of NO leading to mechanisms for ligand substitutions different from those seen for other Lewis-base, diamagnetic ligands.[10] Early studies on the kinetics of nitrosilation of $[Ru^{III}(NH_3)_6]^{3+}$ showed it to be much faster than the replacement of NH_3 by other ligands, suggesting an associative mechanism through a seven-coordinate intermediate, which seems rather unlikely.[11] A few reactions of

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* To whom correspondence should be addressed. E-mail: vaneldik@chemie.uni-erlangen.de (R.v.E.).

[†] University of Erlangen-Nürnberg.

[‡] University of Buenos Aires.

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NO have been more recently studied, particularly with metalloporphyrins.[12,13] The interest is associated with the mechanisms of NO uptake and release at the active sites of metalloenzymes or, more generally, at biologically relevant iron or cobalt metal centers.[14] The more recent studies suggest that dissociation of water from the transition metal center controls the complex-formation mechanisms of Fe(III) porphyrins.[15] With the Fe(II) porphyrins, the rates are much faster, near diffusion controlled.[10] The dissociation reactions in Fe porphyrins are less well understood,[10,12] particularly for the pentacoordinate Fe^{II} porphyrins, for which NO dissociation has been shown to depend strongly on the porphyrin environment.[16] In much of these studies, the complexes may adopt high-spin or low-spin configurations according to the coligands, with the prediction that NO coordination may eventually be associated with a change in the spin state of the {MNO} moieties.[10,17]

Sodium nitroprusside (NP) is used as a vasodilator.[1−3,7] It releases NO thermally in the biological fluids, thus promoting the activation of enzymatic processes associated with diverse physiological functions.[2] The mechanism of NO release is not completely understood yet, although strong evidence exists on the participation of reductants such as thiolates.[18−21] On the other hand, NO can be photoreleased upon visible irradiation of NP, with formation of the $[Fe^{III}(CN)_5H_2O]^{2-}$ ion as the other main primary product.[22]

We present a detailed mechanistic investigation of the formation of NP in the reaction of $[Fe^{III}(CN)_5H_2O]^{2-}$ with NO. Ligand substitution reactions in Fe(II) cyano complexes have been widely studied, but in the case of Fe(III) complexes, information is available for only a few ligands.[23] These reactions are in general very slow and usually occur via a catalytic path involving the corresponding Fe(II) complexes.[24,25] Given the ability of free and bound NO toward redox interconversions,[21] we investigated alternative complex-formation mechanisms that are associated with the redox abilities of the reaction partners.

Experimental Section

Materials. $K_3[Fe^{III}(CN)_5NO_2]$ was prepared as described in the literature.[26] The purity was checked by elemental analysis, UV−vis, and IR spectroscopy and by its reactions in alkaline and acidic medium. NO was purchased from Alpha Gaz in a purity of at least 99.5% and cleaned from traces of higher nitrogen oxides by passing through an Ascarite II column (NaOH on silica gel, Sigma-Aldrich). $Na_3[Fe^{II}(CN)_5NH_3]\cdot 6H_2O$ was obtained from Aldrich. MPz^+ iodide ($MPz^+ = N$-methylpyrazinium ion) was prepared by published procedures.[27] Mercaptosuccinic acid, $NaClO_4$, NaSCN, pyridine (py), pyrazine (pz), and other chemicals necessary for preparing buffer solutions were of analytical grade, and were used without further purification. Solutions were prepared using distilled and purified water (Milli-Q system).

General Procedures. $[Fe^{III}(CN)_5H_2O]^{2-}$ was prepared in solution through the hydrolysis of $K_3[Fe^{III}(CN)_5NO_2]$.[28] A 34 mg amount of the latter salt and 15 mg of NaOH were dissolved in 10 mL of water. After 2 h the solution changed color from red to yellow and was poured into a 100 mL volumetric flask containing the necessary amount of $NaClO_4$ and components of the buffer system. The pH was adjusted with a Mettler Delta 340 pH meter, and a mother solution (1 mM) was prepared through appropriate dilution. This was diluted eventually with the proper buffer or acid solutions. These solutions were never used longer than 8 h; within this period of time reproducible results could be obtained. NO concentrations were calculated from the concentration of a saturated solution, which is known from earlier studies on similar systems, viz. 1.8 mM at 25 °C. This procedure was checked by direct concentration measurements using an NO electrode system.[13,14]

Preliminary experiments were performed for the reaction between $[Fe^{III}(CN)_5H_2O]^{2-}$ and NO. Samples of the mother solution of $[Fe^{III}(CN)_5H_2O]^{2-}$ were deoxygenated with nitrogen for 15 min in a 1 cm quartz cuvette directly attached to a round flask with a sideway gas connection. NO was then bubbled for 2 min. Spectral changes were measured on a Hewlett-Packard 8542A diode array spectrophotometer. The reaction was studied under different conditions, namely by changing either the initial complex concentration (by dilution of the mother solution, range 0.09−1.0 mM) or the pH (4.7 and 3.0). The influence of free nitrite concentration was explored in the range 5−100 mM at pH 4.5. The studies were generally performed at $I = 0.1$ M ($NaClO_4$), with complementary measurements at $I = 0.05$ M, and $T = 25.0$ °C. The possible influence of $[Fe^{II}(H_2O)_6]^{2+}$ (0.1 M) was checked by performing an independent experiment at pH 3.0 with all other variables remaining constant.

Identification and Quantification of the Reaction Product of $[Fe^{III}(CN)_5H_2O]^{2-}$ and NO. A 100 mg amount of $K_3[Fe^{III}(CN)_5NO_2]$ was treated in alkaline medium as described above, followed by the addition of $HClO_4$ to pH 2.5. The final volume of the solution was 100 mL. This was deoxygenated for 1 h, and NO was bubbled for 15 min. After 2 h the last procedure was repeated. After 1 day, the pH was adjusted to 4.5 and the volume was reduced to 5−10 mL. For comparison, a solution of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (NP)

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of approximately the same concentration was prepared. The IR spectra of both solutions were recorded using a Perkin-Elmer liquid cell (with CaF_2 windows and a spacer of 0.2 mm) on an ATI Mattson Infinity FT IR 9495-120-12500 spectrometer. A quantitative determination was done by preparing a 1.21 mM solution of $[Fe^{III}(CN)_5H_2O]^{2-}$ (pH 3, $HClO_4$; 0.1 M $NaClO_4$), which was deoxygenated and treated with NO. After 1 day, nitrogen was bubbled through the solution to eliminate excess NO, and the solution was diluted to 1:5 with the acid solution. Standard solutions of NP in the concentration range 0.12−0.95 mM were prepared (pH 3,0 $HClO_4$; 0.1 M $NaClO_4$). The reagent consisted of a solution of 11.6 g of NaCl, 1.06 g of Na_2CO_3, 0.618 g of H_3BO_3, and 0.15 g of mercaptosuccinic acid in 100 mL, at pH 10.0. All the solutions were previously deoxygenated before mixing. Equal volumes of the NP or sample solutions were mixed with the reagent. The absorbance of the red, stable adduct formed between NP and mercaptosuccinic acid (λ_{max}, 526 nm, $\epsilon = 5800\ M^{-1}\ cm^{-1}$)[29] was used to produce a calibration curve. Thus, the amount of NP formed during the reaction could be determined.

A complementary study was performed to check the stability of the reaction product toward dissociation. The experiments were performed in a 0.88-cm quartz tandem cuvette, in which the NP solution was placed in one compartment and a scavenger solution in the other. The solutions were mixed after temperature equilibration. Spectra were recorded on a Hewlett-Packard 8542A diode array spectrophotometer. All the solutions were deoxygenated and handled in a similar way as described above. The reaction conditions were pH 3.0 ($HClO_4$), $I = 0.1$ M ($NaClO_4$), and $T = 25.0$ °C. Different scavenger solutions were used, containing either $[Fe^{II}(EDTA)(H_2O)]^{2-}$, $[Ru^{III}(EDTA)(H_2O)]^{-}$, or $[Fe^{III}(TMPS)(H_2O)_2]^{3-}$ (where EDTA = ethylenediaminetetraacetate and TMPS = *meso*-tetrakis[sulfonatomesityl]porphine). These have been shown to be efficient trapping compounds for displacing NO from the products of the reactions of NO with metalloporphyrins[13] and other metal chelates.[14] Finally, an experiment using $KMnO_4$ as a reagent for the product of the reaction was also performed.

Kinetic Studies. Kinetic measurements were performed spectrophotometrically, as described below, under pseudo-first-order conditions, with at least a 9-fold excess of NO over the complex concentration, predominantly at pH 3.0 ($HClO_4$) and $I = 0.1$ M ($NaClO_4$). Volumes of 20 mL each of the complex and acid solutions were deoxygenated for 15−20 min, after which NO was bubbled through the acid solution for 5 min. These operations were carried out in Schlenk tubes. Gastight syringes were used to take the required volumes of each solution, to mix them, and to put the resulting sample in a 1.5-cm quartz pillbox optical cell. The NO concentration dependence of the reaction was studied at 25.5 ± 0.1 °C and ambient pressure, for a complex concentration in the range 0.035−0.1 mM and a NO concentration in the range 0.23−1.8 mM. For the temperature and pressure dependence studies, the complex concentration was 0.1 mM and the NO concentration was 0.9 mM. The pressure dependence was studied in a homemade high-pressure unit described elsewhere,[30] at 25.5 ± 0.1 °C in the range 100−1300 bar. The temperature dependence was studied at ambient pressure, in the range 10.0 to 45.0 °C. Spectral changes were recorded with a Shimadzu UV-2101 PC spectrophotometer. The observed rate constant, k_{obs} (s^{-1}), was obtained by fitting the kinetic traces at 394 nm to a single exponential function by means of a Microsoft Excel Solver. All measurements were repeated at least two times, and reported values are the average of at least two measurements, which did not differ more than 10%, usually less than 5%. The error was estimated from the standard deviation of these measurements. The validity of the first-order model was checked with the SPECFIT program,[31] by considering the complete set of spectral changes. The values of k_{obs} obtained in this way did not differ significantly from the one obtained with the single-wavelength procedure.

Studies on the $[Fe^{III}(CN)_5H_2O]^{2-}$/NO Reaction in the Presence of NCS^- or pz. A 0.2 mM solution of $[Fe^{III}(CN)_5H_2O]^{2-}$ was mixed with an equal volume of a perchloric acid solution of NaSCN or pz, in the concentration range 2−50 mM, (final pH 3.0, $I = 0.1$ M). Both solutions were previously deoxygenated, and the latter one was saturated with NO. The mixtures were transferred to a 1-cm quartz cuvette anaerobically. Spectral changes were recorded on a Varian Cary 5G spectrophotometer. Kinetic traces recorded at 394 nm were fitted to a single exponential, as described above. All measurements were performed at 25.0 °C. The conversion of $[Fe^{III}(CN)_5H_2O]^{2-}$ into $[Fe^{III}(CN)_5SCN]^{3-}$ was estimated from the absorbance changes at the corresponding maxima at 394 and 590 nm ($\epsilon = 750$[32] and 2680 $M^{-1}\ cm^{-1}$,[24] respectively).

Reactions of Other $[Fe^{III}(CN)_5L]^{n}$- Complexes with NO ($L = py, NCS^-, CN^-, NO_2^-$). For the complexes with the first two L ligands, the experiments were performed at 25.0 °C, $I = 0.1$ M ($NaClO_4$), and pH 5.0 (10 mM acetate buffer). The solutions were prepared in the following way: 27 mg of $Na_3[Fe^{II}(CN)_5NH_3]\cdot 6H_2O$ was dissolved in 100 mL of deoxygenated buffer solution. After 5 min, a 10-fold excess of py or KSCN was added, and 15 min later, a slight excess of bromine over the stoichiometric requirement was added to oxidize the Fe(II) complex to the corresponding Fe(III) ones. A few minutes later, the excess of bromine was eliminated by bubbling nitrogen through the solution for 30 min. These solutions, approximately 1 mM in Fe(III), were diluted with the buffer solution and used in the measurements. The NO solution was prepared using the same buffer. All solutions were deoxygenated as described above and handled under oxygen-free conditions. At least a 9-fold excess of NO with respect to the complex concentration was employed. A 1 cm quartz cuvette and a Varian Cary 5G spectrophotometer were used for the measurements. Kinetic data were analyzed by the SPECFIT program. For the reaction of $[Fe^{III}(CN)_5py]^{2-}$ with NO, a two exponential model was used to fit the data. The yield of NP was determined through the reaction with mercaptosuccinic acid as described above. The reactions of 0.1 mM $[Fe^{III}(CN)_5NO_2]^{3-}$ and 0.1 mM $[Fe^{III}(CN)_6]^{3-}$ with 0.9 mM NO were studied at pH 5.0 (10 mM acetate buffer), $I = 0.1$ M ($NaClO_4$), and $T = 25.0$ °C.

Results and Discussion

The reaction of interest can be formulated in principle as the equilibrium reaction 1, where k_f represents the forward rate constant for complex formation and k_d corresponds to the reverse rate constant comprising the dissociation of the NO ligand.

$$[Fe^{III}(CN)_5H_2O]^{2-} + NO \underset{k_d}{\overset{k_f}{\rightleftarrows}} [Fe(CN)_5NO]^{2-} + H_2O \quad (1)$$

Under pseudo-first-order conditions the observed rate con-

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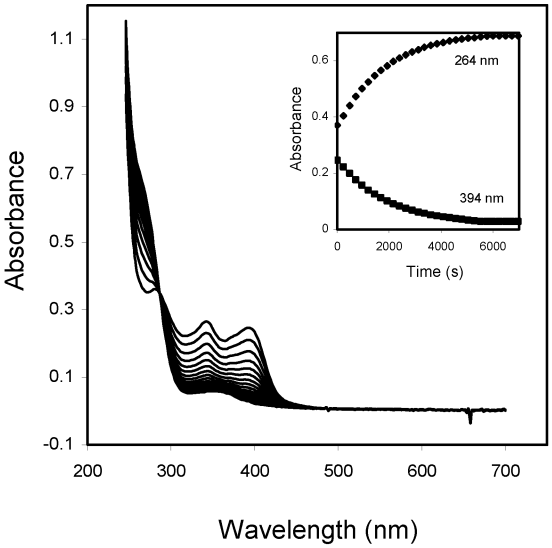

Figure 1. Spectral changes recorded during the reaction of $[Fe^{III}(CN)_5H_2O]^{2-}$ with NO. $[Fe^{III}(CN)_5H_2O^{2-}] = 0.25$ mM, [NO] = 1.8 mM, pH = 4.7 (5 mM acetate buffer), $I = 0.1$ M ($NaClO_4$), $T = 25.0$ °C, and cycle time 360 s. Inset: Absorbance−time traces at 264 and 394 nm, $k_{obs} = 5.2 \times 10^{-4}$ s^{-1}.

stant, k_{obs}, should depend linearly on the NO concentration according to eq 2, with a slope equal to k_f and an intercept equal to k_d.

$$k_{obs} = k_f[NO] + k_d \tag{2}$$

Figure l shows a typical kinetic experiment at pH 4.7. The two characteristic bands of $[Fe^{III}(CN)_5H_2O]^{2-}$ at 394 and 340 nm [32] disappear during the reaction while a new band appears at 264 nm with an isosbestic point at 286 nm. The inset of Figure 1 reveals a pseudo-first-order behavior for the decrease of the reactant concentration at 394 nm, as well as for the increase of the product at 264 nm. The band at 264 nm corresponds to a reported value for NP.[33]

The IR spectrum of the product of reaction 1 was found to be identical to the one obtained for a pure sample of NP. It showed characteristic bands at 1938 and 2144 cm^{-1} associated with ν_{NO} and ν_{CN} stretchings, respectively.[34] The reaction product was found to react with mercaptosuccinic acid in the same way as pure NP, with a yield of 99% for reaction 1.

We carefully checked the influence of different factors on k_{obs}. Table 1 summarizes the results obtained under different conditions (see Experimental Section).

It can be seen that k_{obs} is nearly independent of the initial complex concentration at pH 4.7 and 3.0. The results allow us to conclude that there is no dimerization of $[Fe^{III}(CN)_5H_2O]^{2-}$ occurring under our experimental conditions (or that it is sufficiently slow on our reaction time scale),[24] since if this was the case k_{obs} would decrease significantly with increasing complex concentration. There is some increase in k_{obs} on increasing the free nitrite concentration, but the effect is very small (≤10%), from which we conclude that the free nitrite in solution that originated from the starting compound, $[Fe^{III}(CN)_5NO_2]^{3-}$, or from impurities in the NO gas has no significant influence on the reaction under study. However, at nitrite concentrations higher than 50 mM, kinetic traces were no longer single exponentials and significant deviations were observed. The ionic strength of the solution has no appreciable effect on the value of k_{obs}, which is consistent with a reaction involving an uncharged reaction partner. There is also no effect of the pH of the solution in the range 3.0−4.7. A similar experiment at pH 2.0 also showed no influence under the selected conditions. Finally, the presence of 0.1 mM Fe(II) did not interfere appreciably with the reaction. It was found before that Fe(II) may catalyze substitution reactions in Fe(III) systems,[24,25] which is apparently not the case in this study.

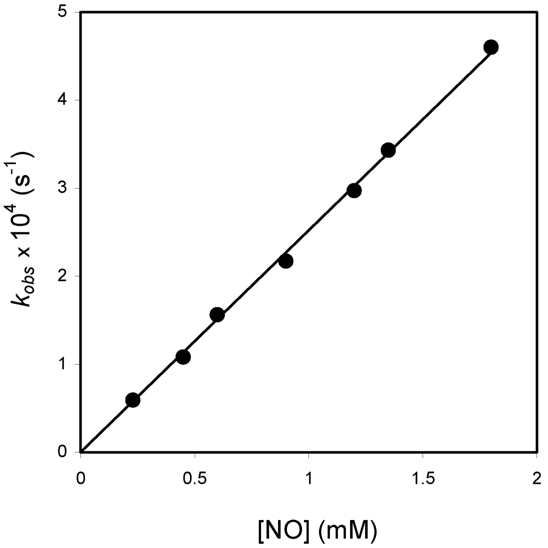

Figure 2. NO concentration dependence for the complex-formation reaction. $T = 25.5 \pm 0.1$ °C, pH = 3.0 ($HClO_4$), $I = 0.1$ M ($NaClO_4$), $[Fe^{III}(CN)_5H_2O^{2-}] = 0.1-0.035$ mM, [NO] = 1.8−0.23 mM. $k_f = 0.252 \pm 0.004$ M^{-1} s^{-1}, and $R^2 = 0.999$.

Table 1. Kinetic Data Obtained in a Series of Preliminary Experiments

$[Fe^{III}(CN)_5H_2O]$ (mM)	pH	$[NO_2^-]$ (mM)	$[NaClO_4]$ (mM)	$[Fe^{II}]$ (mM)	10^4k_{obs} (s^{-1})
0.094	4.7				5.0
0.25	4.7				5.2
0.50	4.7				4.9
0.75	4.7				5.2
0.99	4.7				5.1
1.00	3.0				5.0
0.50	3.0				5.3
0.25	3.0				5.5
0.70	3.0				5.0
0.46	4.5	5			5.0
0.46	4.5	10			5.4
0.46	4.5	25			5.4
0.46	4.5	35			5.5
0.46	4.5	50			5.6
0.33	4.5		50		5.5
0.33	4.5		100		5.6
0.56	3.0			0.1	5.9

Kinetic Analysis of Reaction 1. Figure 2 shows that k_{obs} varies linearly with the concentration of NO. From the slope, k_f was found to be 0.252 ± 0.004 M^{-1} s^{-1} at 25.5 ± 0.1 °C. Figure 2 shows no meaningful intercept, from which it follows that k_d is negligible under the selected experimental conditions. This is entirely consistent with NP being an

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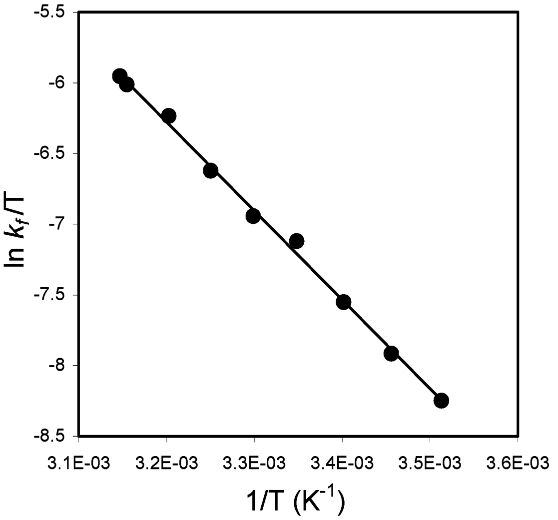

Figure 3. Eyring plot for the complex-formation rate constant (k_f). [NO] = 0.9 mM, [$Fe^{III}(CN)_5H_2O^{2-}$] = 0.1 mM, pH = 3.0 ($HClO_4$), I = 0.1 M ($NaClO_4$), T = 10−45 °C, $\Delta H^{\ddagger} = 52 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -82 \pm 4$ J K^{-1} mol^{-1}, and $R^2 = 0.997$.

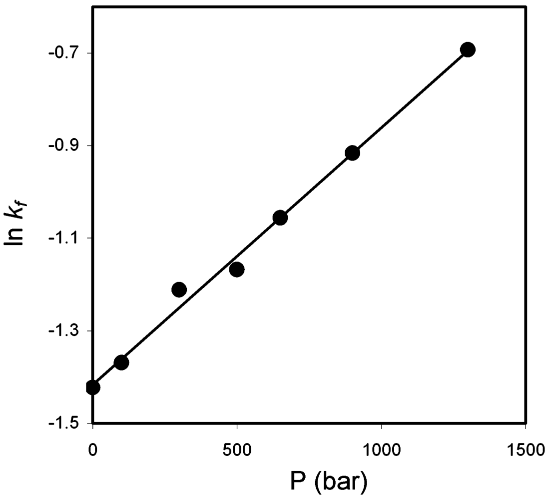

Figure 4. Plot of ln k_f versus pressure. [NO] = 0.9 mM, [$Fe^{III}(CN)_5$-H_2O^{2-}] = 0.1 mM, pH = 3.0 ($HClO_4$), I = 0.1 M ($NaClO_4$), $T = 25.5 \pm 0.1$ °C, pressure = 1−1300 bar, $\Delta V^{\ddagger} = -13.9 \pm 0.5$ cm^3 mol^{-1}, and $R^2 = 0.993$.

Table 2. Kinetic Data for the Complex-Formation Reaction (pH 3.0; I = 0.1 M)

[$Fe^{III}(CN)_5H_2O$] (mM)	[NO] (mM)	T (°C)	P (bar)	$10^4 k_{obs}$ (s^{-1})
0.035	0.23	25.5	1	0.59 ± 0.01
0.06	0.45	25.5	1	1.08 ± 0.08
0.09	0.60	25.5	1	1.56 ± 0.06
0.10	0.90	25.5	1	2.17 ± 0.05
0.10	1.20	25.5	1	2.97 ± 0.03
0.10	1.35	25.5	1	3.43 ± 0.05
0.10	1.80	25.5	1	4.6 ± 0.2
0.10	0.90	11.5	1	0.67 ± 0.05
0.10	0.90	16.2	1	0.95 ± 0.05
0.10	0.90	20.8	1	1.39 ± 0.03
0.10	0.90	30.0	1	2.63 ± 0.08
0.10	0.90	34.5	1	3.68 ± 0.01
0.10	0.90	39.1	1	5.5 ± 0.2
0.10	0.90	43.8	1	6.99 ± 0.05
0.10	0.90	44.6	1	$7.42 + 0.05$
0.10	0.90	25.5	100	$2.29 + 0.05$
0.10	0.90	25.5	300	2.68 ± 0.02
0.10	0.90	25.5	500	2.80 ± 0.03
0.10	0.90	25.5	650	3.13 ± 0.02
0.10	0.90	25.5	900	3.6 ± 0.1
0.10	0.90	25.5	1300	4.5 ± 0.1

extremely stable product toward NO dissociation, given the well-characterized Fe−N multiple bond. The properties of NP also anticipate that a significant charge transfer between the initial reactants has occurred in reaction 1. NP is a complex with a $\{FeNO\}^6$ configuration (in the Enemark−Feltham formalism),[35] and its different spectroscopic properties and diamagnetic character allow it to be described as a species containing formally Fe(II) and NO^+. The latter is a limiting idealized situation used for complexes involving NO acting as a three-electron donor toward the metal, with a triple N−O bond order and a high value of ν_{NO} (usually greater than 1900 cm^{-1}).[1] For these reasons, negative results were obtained in the experiments with trapping agents for bound nitrosyl. The latter experiments were found to be successful for measuring NO formation and dissociation rates from metallonitrosyl complexes containing porphyrin and chelate ligands.[13,14] Thus, k_d values for several reactions similar as 1 showed values around 10^1−10^3 s^{-1}. This already suggests that the binding of NO in the products of these reactions is not so strong as in NP, probably involving less charge transfer from NO to the metal upon coordination. Another evidence for the NO^+ character of the nitrosyl ligand in NP is given by the negative test with permanganate, which, on the other hand, is certainly reduced by free NO.

Figures 3 and 4 display the temperature and pressure dependence of reaction 1, respectively. The activation parameters were estimated to be $\Delta H^{\ddagger} = 52 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -82 \pm 4$ J K^{-1} mol^{-1}, and $\Delta V^{\ddagger} = -13.9 \pm 0.5$ cm^3 mol^{-1}. Table 2 summarizes all kinetic data.

Suggested Mechanism. Some of the few studies in the literature on substitution reactions of $[Fe^{III}(CN)_5H_2O]^{2-}$ [23] allow for a comparison with our system. Several entering ligands have been used, namely NCS^-, N_3^-, $[Co(CN)_6]^{3-}$,[24] and diverse nucleosides.[25] In general it was found that such substitution reactions are very slow, with second-order rate constants in the range 10^{-4}−10^{-7} M^{-1} s^{-1} at 25 °C. Interestingly, these reactions are catalyzed by Fe(II) or other reductant species, it being proposed that previous reduction of the Fe(III) center is needed for obtaining faster reactivities, associated with the greater lability of water from the Fe(II) centers compared to the Fe(III) ones. For the reactions of $[Fe^{III}(CN)_5H_2O]^{2-}$ with the nucleosides cytosine, cytidine, and cytidine-5'-monophosphate,[25] the second-order rate constants were around 10^{-4} M^{-1} s^{-1} at 35 °C. Activation entropies and volumes were in the range 5−120 J K^{-1} mol^{-1} and 3−6 cm^3 mol^{-1}, respectively. These data were analyzed as consistent with a dissociative interchange (I_d) mechanism, suggesting that this is generally valid for ligand substitution reactions on $[Fe^{III}(CN)_5H_2O]^{2-}$.[25] Kinetic results for the fast complex-formation reactions of NO with high-spin Fe(III) metalloporphyrins also suggest that the dissociative release of water is rate-controlling.[10,13,15]

In contrast with the above behavior, we find that k_f in eq 1 is many orders of magnitude higher than the values quoted

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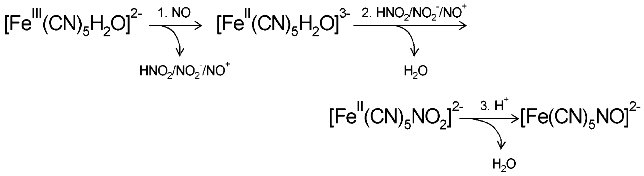
(35) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

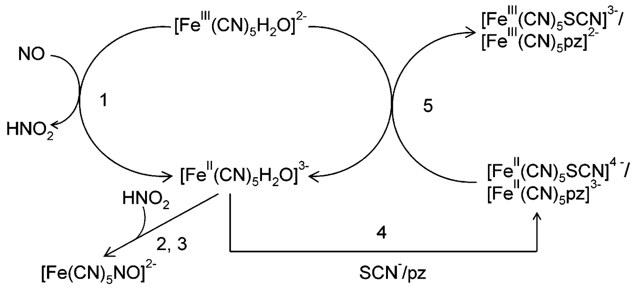
Scheme 1



above. Also, contrasting results appear for both $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$, which show negative values. On the basis of these differences, we suggest that reaction 1 involves a rate-determining outer-sphere electron-transfer reaction, which produces $[Fe^{II}(CN)_5H_2O]^{3-}$ and is followed by fast complex-formation reactions with the ligands present in the medium to produce NP, as shown in Scheme 1.

No direct spectral evidence on the intermediacy of $[Fe^{II}(CN)_5H_2O]^{3-}$ was found in these experiments. The rate of water exchange in the latter complex is ca. 300 s^{-1},[23,36] and thus it may react rapidly with different ligands. One possibility is that the product of the slow step 1, NO^+, could bind with an expected rate constant of ca. 600 M^{-1} s^{-1} (by comparison with the measured rate with MPz^+).[27] However, it has been shown that NO^+ is highly reactive in water (estimated lifetime 3×10^{-10} s), producing HNO_2 (with $K = [NO^+]/[HNO_2][H^+] = 10^{-6.5}$).[37] Thus, the HNO_2/NO_2^- species (depending on pH) may coordinate to $[Fe^{II}(CN)_5H_2O]^{3-}$ with rate contants of around 300 and 40 M^{-1} s^{-1}, respectively, to give $[Fe^{II}(CN)_5NO_2]^{4-}$.[23] The differences in the values of these rate constants have been interpreted in terms of the charges influencing the ion-pair equilibrium preceding the coordination step.[38] We conclude that, under our reaction conditions, step 2 must be at least 1 order of magnitude faster than step 1. Although not explicitly included in Scheme 1, another possibility must be considered, namely the coordination of NO to $[Fe^{II}(CN)_5H_2O]^{3-}$. The concentration of NO is 1 order of magnitude greater than the above-discussed entering ligands and should, in principle, lead to the $[Fe^{II}(CN)_5NO]^{3-}$ ion, which is a well-characterized species.[39] The latter intermediate is, however, not observed. The experiments with pz as a scavenger for $[Fe^{II}(CN)_5H_2O]^{3-}$, which are described below, suggest that NO cannot compete with NO_2H present in the second coordination sphere, because of its low concentration (NO should bind with a rate constant similar to pz). In addition, step 3 is reported in the literature to be a very fast reaction at pH 5.[40,41] From a comparison of these data with the observed rate constants in Table 2 and Figure 2, it follows that steps 2 and 3 in Scheme 2 cannot be rate-controlling processes. This is also consistent with the fact that no intermediates were detected.

Scheme 2



Finally, an earlier study on the reduction of $[Fe^{III}(CN)_5NO_2]^{3-}$ with ascorbic acid[42] reported the formation of NP in an outer-sphere electron-transfer mechanism. The reported $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values, viz. -119 J K^{-1} mol^{-1} and -10 cm^3 mol^{-1}, respectively, are very close to those found for k_f in this study. These activation parameters can be accounted for in terms of an increase in electrostriction due to significant charge concentration during the electron-transfer process. The outer-sphere reduction of $[Fe^{III}(CN)_6]^{3-}$ with ascorbic acid also exhibits very similar activation parameters.[42]

The redox potential of the $[Fe^{III}(CN)_5H_2O]^{2-}$ complex is 0.37 V,[43] and the value for the HNO_2/NO couple at pH 3.0 is 0.81 V ($E° = 0.98$ V, all values vs NHE).[44] The reason the observed reaction is still a spontaneous process at this pH must be related to the fact that the rapid subsequent formation of NP drives the reaction. The equilibrium constant for the formation of NP from $[Fe^{II}(CN)_5NO_2]^{4-}$ is 5×10^{23} M^{-2}.[40,41] In fact, it is worth to point out that the reverse of reaction 1 needs photochemical activation.[22]

In an attempt to gain more evidence in favor of the proposed mechanism, we report below on studies performed in the presence of added reactants able to scavenge the intermediate $[Fe^{II}(CN)_5H_2O]^{3-}$ complex produced in the rate-determining electron-transfer step, in a similar way as previously discussed for the species appearing in Scheme 1. In addition, the reactions of other $[Fe^{III}(CN)_5L]^{n-}$ complexes with NO have also been studied.

Complex-Formation Reactions in the Presence of NCS^- and pz. Figure 5 presents the repetitive scan spectra recorded for the reaction of $[Fe^{III}(CN)_5H_2O]^{2-}$ with NO in the presence of SCN^-. The band near 394 nm decreases,[45] and a new band appears at 598 nm with isosbestic points at 290 and 446 nm. The first isosbestic point and the absorption increase at lower wavelengths reflect the formation of NP as previously shown in Figure 1. Furthermore, the band at 598 nm is characteristic of the $[Fe^{III}(CN)_5NCS]^{3-}$ complex.[24] SPECFIT analysis revealed only two components and a first-order process. The inset of Figure 5 shows that the observed rate constant, k_{obs}, depends linearly on the thiocyanate concentration, with a slope of $(2.3 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1} and an intercept of

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(36) Toma, H. E.; Batista, A. A.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 7509.

(37) Ridd, J. H. *Adv. Phys. Org. Chem.* **1979**, *16*, 1.

(38) Bradic, Z.; Pribanic, M.; Asperger, S. *J. Chem. Soc., Dalton Trans.* **1975**, 353.

(39) Cheney, R. P.; Simic, M. G.; Hoffman, M. Z.; Taub, I. A.; Asmus, K. D. *Inorg. Chem.* **1977**, *16*, 2187.

(40) Masek, J.; Wendt, H. *Inorg. Chim. Acta* **1969**, *3*, 455.

(41) Maciejoska, I.; Stasicka, Z.; Stochel, G.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1999**, 3643.

(42) Wanat A.; van Eldik, R.; Stochel, G. *J. Chem. Soc., Dalton Trans.* **1998**, 2497.

(43) Ilkowska, E.; Lewinski, K.; van Eldik, R.; Stochel, G. *J. Biol. Inorg. Chem.* **1999**, *4*, 302.

(44) Ball, M. C.; Norbury, A. H. *Physical Data for Inorganic Chemists*; Longman: Essex, U.K., 1974.

(45) The 390 nm band is obscured by typical NO_2H absorptions appearing in the UV region, for experiments made at pH 3.0. This complication still allowed reliable kinetic measurements.

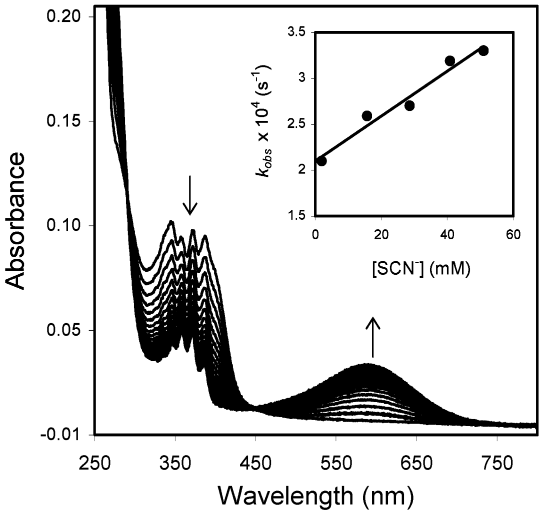

Figure 5. Spectral changes recorded during the reaction of $[Fe^{III}(CN)_5H_2O]^{2-}$ with NO in the presence of thiocyanate. $[SCN^-] = 51$ mM, $[Fe^{III}(CN)_5H_2O^{2-}] = 0.1$ mM, $[NO] = 0.9$ mM, pH = 3.0 ($HClO_4$), $I = 0.1$ M ($NaClO_4$), $T = 25.0$ °C, $k_{obs} = 3.30 \times 10^{-4}$ s^{-1}, and cycle time 480 s. Inset: Thiocyanate concentration dependence for the observed rate constant (k_{obs}), with slope = $(2.3 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1}, intercept = $2.17 \pm 0.08 \times 10^{-4}$ s^{-1}, and $R^2 = 0.969$.

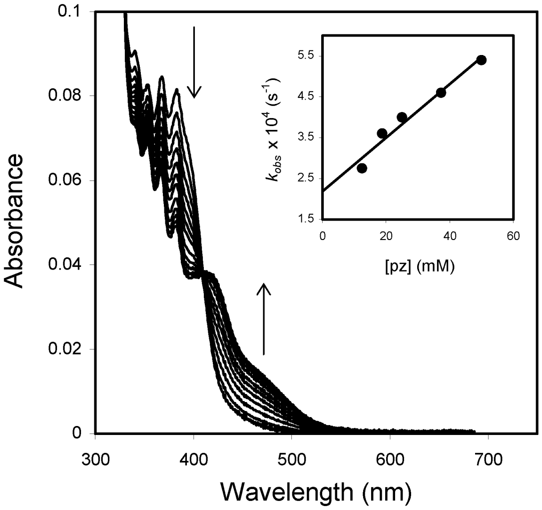

Figure 6. Spectral changes recorded during the reaction of $[Fe^{III}(CN)_5H_2O]^{2-}$ with NO in the presence of pyrazine. [pyrazine] = 18.8 mM, $[Fe(CN)_5H_2O^{2-}] = 0.1$ mM, $[NO] = 0.9$ mM, pH = 3.0 ($HClO_4$), $I = 0.1$ M ($NaClO_4$), $T = 25.0$ °C, $k_{obs} = 3.60 \times 10^{-4}$ s^{-1}, and cycle time = 480 s. Inset: Pyrazine concentration dependence for the observed rate constant, k_{obs}, with slope = $(6.5 \pm 0.7) \times 10^{-3}$ M^{-1} s^{-1}, intercept = $(2.2 \pm 0.2) \times 10^{-4}$ s^{-1}, and $R^2 = 0.965$.

$(2.17 \pm 0.08) \times 10^{-4}$ s^{-1} at 25 °C. The degree of conversion of $[Fe^{III}(CN)_5H_2O]^{2-}$ to $[Fe^{III}(CN)_5NCS]^{3-}$ was found to increase with increasing thiocyanate concentration. It is important to note that the reaction between $[Fe^{III}(CN)_5H_2O]^{2-}$ and SCN^- under similar conditions but in the absence of NO is orders of magnitude slower.[24]

The reaction of $[Fe^{III}(CN)_5H_2O]^{2-}$ with NO in the presence of pz exhibits a very similar behavior, and the observed spectral changes are shown in Figure 6. Absorption bands near 394 nm decrease again, along with a new band appearing at 415 nm, with a shoulder at 455 nm and an isosbestic point at 411 nm. SPECFIT analysis also revealed a first-order process. Some decomposition of the products seems to occur along with nearly completion of the reaction. The intensity of the new band and shoulder increases with increasing pz concentration. The observed rate constant also depends linearly on the pz concentration, as shown in Figure 6, with a slope of $(6.5 \pm 0.7) \times 10^{-3}$ M^{-1} s^{-1} and an intercept of $(2.2 \pm 0.2) \times 10^{-4}$ s^{-1}. In the absence of NO, the observed spectral changes under the same conditions are negligible. The band at 415 nm can be assigned to $[Fe^{III}(CN)_5pz]^{2-}$,[46] whereas the shoulder at 455 nm corresponds to $[Fe^{II}(CN)_5pz]^{3-}$.[27]

To account for these results, we propose the catalytic mechanism presented in Scheme 2. NCS^- or pz may compete with HNO_2/NO_2^- to react with the intermediate $[Fe^{II}(CN)_5H_2O]^{3-}$ complex. The resulting $[Fe^{II}(CN)_5NCS]^{4-}$ and $[Fe^{II}(CN)_5pz]^{3-}$ complexes can be oxidized by $[Fe^{III}(CN)_5H_2O]^{2-}$ to produce the corresponding Fe(III) complexes.[46] Reaction steps 1−3 are the same as in Scheme 1.

Although the $[Fe^{II}(CN)_5H_2O]^{3-}$ intermediate could not be observed directly, evidence for its competitive reaction with NCS^- is obtained through formation of the well-characterized $[Fe^{III}(CN)_5NCS]^{3-}$ ion (reactions 4 and 5). On the assumption that the Fe^{II} complexes exist in steady state, eq 3 can be derived for SCN^- or pz as scavenger, where k_2 and k_4 represent the rate constants for steps 2 and 4 in Scheme 2, respectively. The rate law predicts a linear dependence of k_{obs} on the thiocyanate (or pyrazine) concentration, in agreement with that shown in the insets of Figures 5 and 6. Furthermore, the intercept of these plots should represent k_1[NO], i.e., k_f[NO], and the values cited above are in exact agreement with this prediction.

$$k_{obs} = k_1[NO]\left(1 + \frac{k_4[SCN^-/pz]}{k_2[HNO_2]}\right) \qquad (3)$$

Conclusive evidence for the necessary reduction of the Fe^{III} center as a first step in the reaction with NO is given by the experiment with pyrazine as a competitive scavenger. Here both $[Fe^{II}(CN)_5pz]^{3-}$ and $[Fe^{III}(CN)_5pz]^{2-}$ were detected as reaction intermediates, in contrast to the situation with NCS^-, where only the final oxidized complex was found. This is traced to $[Fe^{II}(CN)_5pz]^{3-}$ being a weaker reductant than $[Fe^{II}(CN)_5NCS]$,$^{4-}$ [27] thus preventing the complete oxidation by $[Fe^{III}(CN)_5H_2O]^{2-}$. Under these conditions the approximations used to derive eq 3 are not fully valid. The value of the second-order rate constant for complex formation of $[Fe^{II}(CN)_5H_2O]^{3-}$ with SCN^- is 64 M^{-1} s^{-1},[38] and the one with pyrazine is 380 M^{-1} s^{-1}.[27] Thus the higher slope observed for the pyrazine concentration dependence shown in Figure 6, as compared to that for the thiocyanate concentration dependence in Figure 5, is in qualitative agreement with these rate constants. The fact that not all of the $[Fe^{II}(CN)_5pz]^{3-}$ is oxidized to the Fe(III) complex may account for the failure of a quantitative agreement. All the kinetic data for these reactions are summarized in Table 3. Some experiments were also performed using MPz^+ to scavenge the $[Fe^{II}(CN)_5H_2O]^{3-}$ species. It was found that

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(46) Toma, E. H.; Malin, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 288.

Table 3. Kinetic Data for the Complex-Formation Reaction in the Presence of SCN^- and Pyrazine ($[Fe^{III}(CN)_5H_2O^{2-}] = 0.1$ mM; [NO] = 0.9 mM; $I = 0.1$ M, pH 3.0; $T = 25.0$ °C)

[SCN] (mM)	[pz] (mM)	10^4k_{obs} (s^{-1})	[SCN] (mM)	[pz] (mM)	10^4k_{obs} (s^{-1})
2.0	0	2.10 ± 0.05	0	12.5	2.75 ± 0.05
15.7	0	2.59 ± 0.05	0	18.8	3.60 ± 0.08
28.6	0	2.7 ± 0.1	0	25.0	4.0 ± 0.5
40.8	0	3.19 ± 0.05	0	37.3	4.6 ± 0.1
51.0	0	3.3 ± 0.5	0	50.0	5.4 ± 0.1

the $[Fe^{II}(CN)_5MPz]^{2-}$ complex is indeed formed, the reaction behaving similarly as with pyrazine. No detailed studies were pursued because of the apparent reactivity of iodide present in the Mpz^+ compound.

Reaction of Other $[Fe^{III}(CN)_5L]^{n-}$ Complexes with NO (L = py, NCS^-, NO_2^-, CN^-). The proposed mechanism for reaction 1 (Scheme 1) suggests that similar electron-transfer reactions could operate by using other inert $[Fe^{III}(CN)_5L]^{n-}$ complexes. Figure 7a reports the spectral changes observed during the reaction of $[Fe^{III}(CN)_5py]^{2-}$ with NO. The reactant complex has two absorption bands at 368 and 414 nm ($\epsilon = 800$ and 1100 M^{-1} cm^{-1}, respectively).[46] During the reaction with NO, the absorption of the band at 414 nm decreases, whereas the one of the band at 368 nm first increases and then decreases for longer reaction times. SPECFIT analysis revealed evidence for the presence of an intermediate with a band at 364 nm (see Figure 7b). This is consistent with the initial formation of $[Fe^{II}(CN)_5py]^{3-}$ ($\lambda_{max} = 362$ nm, $\epsilon = 3700$ M^{-1} cm^{-1})[27] (see Figure 7c). The latter ϵ value, which is much larger than for the corresponding Fe^{III} complex, explains the initial absorbance increase at 368 nm. The subsequent decrease is ascribed to the aquation reaction, for which $k = 1.1 \times 10^{-3}$ s^{-1} (25 °C).[27] From the initial decay at 414 nm, a pseudo-first-order rate constant of 1.4×10^{-4} s^{-1} can be estimated, a value similar to the one obtained for the reaction of NO with $[Fe^{III}(CN)_5H_2O]^{2-}$. Finally, NP is formed as in the previous reactions, with a yield of 72%. The kinetic behavior of the reaction at longer reaction times appears to be complicated by secondary reactions, during which a broad band, centered at ca. 1200 nm, develops. It can be assigned to the formation of a mixed-valency cyano-bridged dimer $[(NC)_5Fe^{III}(\mu\text{-}NC)Fe^{II}(CN)_4py]^{5-}$, which has been previously characterized.[47] Due to the mentioned complications the SPECFIT analysis can only be interpreted in a qualitative way.

We also studied the reaction between $[Fe^{III}(CN)_5NCS]^{3-}$ and NO. During the reaction the intensity of the band of the reactant at 598 nm decreases and a new broad and intense band appears near 730 nm, with no isosbestic point. The reaction seems to proceed analogously as with py in the first electron-transfer step. However, the formed $[Fe^{II}(CN)_5NCS]^{4-}$ is much more labile toward dissociation, and it is feasible that the aqua ion reacts with the Fe(III) reactant to form a stable mixed-valent cyano-bridged complex, consistent with the absorption at 730 nm. In support of the above explanation, $[Fe^{III}(CN)_5NCS]^{3-}$ was shown to react with $[Fe^{II}(CN)_5$-

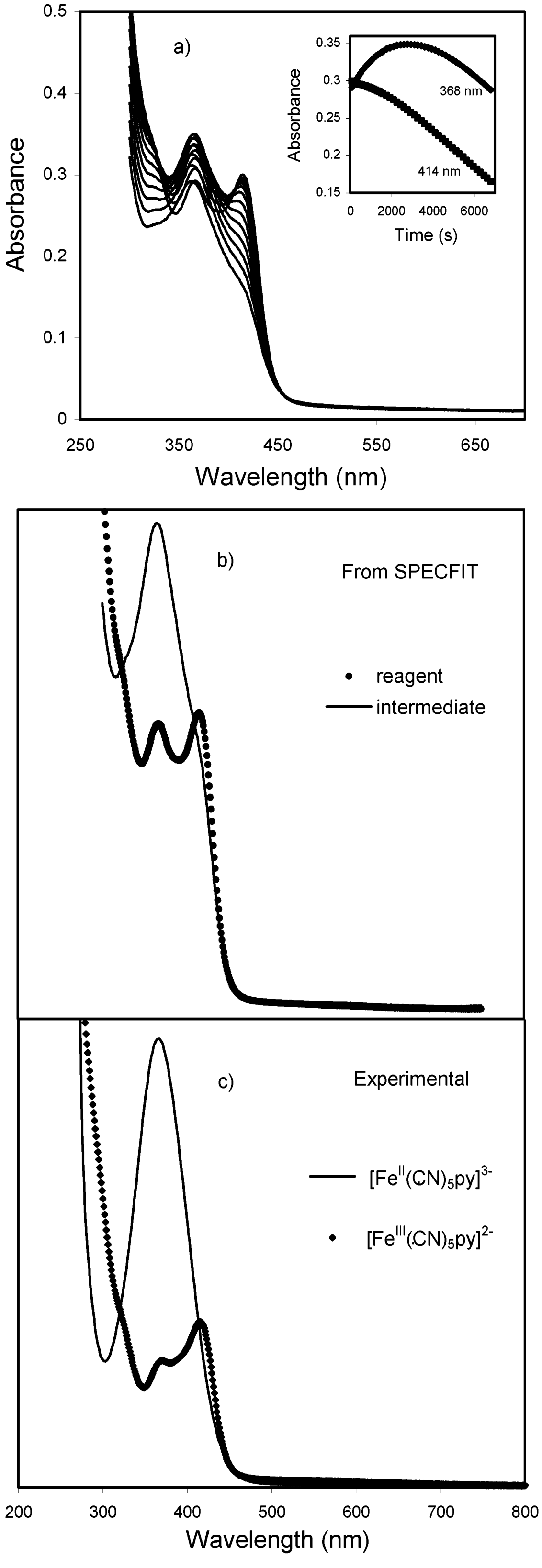

Figure 7. (a) Spectral changes recorded during the reaction of $[Fe^{III}(CN)_5py]^{2-}$ with NO. $[Fe^{III}(CN)_5py^{2-}] = 0.1$ mM, [NO] = 0.9 mM, pH = 5.0 (10 mM acetate buffer), $I = 0.1$ M ($NaClO_4$), and cycle time 336 s. Inset: Absorbance−time traces at 414 and 368 nm. (b) Spectra calculated for the starting compound and the intermediate obtained from SPECFIT analysis. (c) Experimental spectra of $[Fe^{III}(CN)_5py]^{2-}$ and $[Fe^{II}(CN)_5py]^{3-}$.

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(47) Souto, M. F.; Cukiernik, F. D.; Forlano, P.; Olabe, J. A. *J. Coord. Chem.* **2001**, *54*, 343.

$H_2O]^{3-}$ (1 mM Fe(III) and 0.1 mM Fe(II) complex), producing very similar spectral changes. Note that a similar behavior was described above for the reaction of $[Fe^{III}(CN)_5py]^{2-}$. The yield of NP was found to be quite low, viz. 37%.

The reaction between $[Fe^{III}(CN)_5NO_2]^{3-}$ and NO was found to be significantly faster than the previously described reactions, occurring in the stopped-flow time regime, with a yield of 98% for the formation of NP. In contrast, the $[Fe^{III}(CN)_6]^{3-}$ ion showed to be practically unreactive on the time scale of hours.

Although no strictly quantitative results are presently reported for the relevant rate constants, the spectral evolution of all these reactions also agree with an initial electron-transfer step with reduction of the metal center. For L = py and NCS^-, the initial rates appear to be of the same order of magnitude as found for $[Fe^{III}(CN)_5H_2O]^{2-}$. The subsequent reactions of the intermediates relate to the cleavage of the $Fe^{II}-L$ bonds through aquation, which is necessary for the formation of the main final product, NP. As the above complexes have very similar redox potentials for the corresponding Fe(III)/Fe(II) couples,[27,36,43] the similar initial rates point to the confirmation of the already discussed outer-sphere electron-transfer mechanism. Interestingly, the faster formation of NP in the reaction of $[Fe^{III}(CN)_5NO_2]^{3-}$ with NO appears as being consistently related to a direct formation of NP without rupture of the $Fe-NO_2^-$ bond, avoiding the intermediacy of the aqua ion, as was the case in the reduction of $[Fe^{III}(CN)_5NO_2]^{3-}$ with ascorbic acid.[43,48] In the other extreme situation, the very small reactivity of $[Fe^{III}(CN)_6]^{3-}$ (as measured by the slow decay of its absorption band at 418 nm) and the inertness of the $[Fe^{II}(CN)_6]^{4-}$ product toward substitution[23a] explain the absence of NP formation on the time scale of hours.

Conclusions

The complex-formation reaction between $[Fe^{III}(CN)_5H_2O]^{2-}$ and NO was studied in detail, and NP was found to be produced quantitatively. The complex-formation rate constant and the corresponding activation parameters were found *not* to be in agreement with those for typical ligand substitution reactions involving $[Fe^{III}(CN)_5H_2O]^{2-}$. The electronic and structural properties of NP, as well as the rate and activation parameters for the reaction, support a rate-determining, one-electron outer-sphere electron transfer between the reaction partners, with subsequent fast formation of NP after coordination of nitrite or NO_2H, depending on pH. The same reaction in the presence of SCN^-, pz, and MPz^+ clearly demonstrated the formation of $[Fe^{II}(CN)_5H_2O]^{3-}$ as a reaction intermediate. Finally, the reactions of $[Fe^{III}(CN)_5NCS]^{3-}$ and $[Fe^{III}(CN)_5py]^{2-}$ with NO also appear to proceed by similar outer-sphere mechanisms, with intermediate formation of Fe(II) complexes. These require the dissociation of NCS^- or py to form the final stable product, NP. For the latter reason, the hexacyanoferrate(III) ion is unreactive, not leading to NP. The dissociation process is avoided for $L = NO_2^-$, because fast NO_2^- to NO^+ conversion may occur at the metal center without rupture of the Fe−N bond. The mechanism of NO reactivity with all these low-spin Fe(III) metal centers appears as significantly different from the few available studies on NO coordination to high-spin Fe(III) complexes comprising porphyrin and Fe(II) complexes comprising polyaminocarboxylate chelates.[12−15,17] In these cases, coordination seems to operate through the rate-determining dissociation of water from the Fe centers. Also, the dissociation of the bound NO ligand in the product appears as extremely slow for NP, in contrast with the moderately fast NO dissociation processes measured for the chelated metal centers.

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(48) Given the similar value of the standard redox potential of the $[Fe^{III,II}(CN)_5NO_2]^{3-,4-}$ couple compared to other $[Fe^{III,II}(CN)_5L]^{n-}$,[43] a similar rate could be predicted for the electron-transfer step. However, the $NO_2^- \rightarrow NO^+$ conversion at the iron(II) center drives the real potential toward more positive values.