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One-Electron Reduction of Pentacyanonitrosylferrate(II) Ion in Aqueous Solution[1]

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The one-electron reduction of pentacyanonitrosylferrate(II) ion, $Fe(CN)_5NO^{2-}$ (nitroprusside ion), in aqueous solution has been studied using continuous and pulse radiolysis techniques, the latter with optical absorption and kinetic conductivity detection. The reducing radicals e_{aq}^-, CO_2^-, $\cdot CH_2OH$, $(CH_3)_2\dot{C}OH$, and H react with $Fe(CN)_5NO^{2-}$ ($k = 1.0 \times 10^{10}$, 4.0×10^8, 6.7×10^8, 2.9×10^9, and 7×10^7 M^{-1} s^{-1}, respectively) to yield $Fe(CN)_5NO^{3-}$ characterized by an absorption spectrum with λ_{max} 345 and 440 nm (ϵ_{max} 3.5×10^3 and 5.5×10^2 M^{-1} cm^{-1}, respectively); the spectrum is independent of pH (1–8.5). $Fe(CN)_5NO^{3-}$ undergoes first-order decay with the loss of CN^-, presumably from the trans position, to form $Fe(CN)_4NO^{2-}$ (λ_{max} 615 nm, ϵ_{max} 3.8×10^2 M^{-1} cm^{-1}) according to the following reactions: $Fe(CN)_5NO^{3-} \rightleftarrows Fe(CN)_4NO^{2-} + CN^-$, $K = 6.8 \times 10^{-5}$; $CN^- + H^+ \rightleftarrows HCN$, $K = 2.0 \times 10^9$. The observed first-order rate constant for the disappearance of $Fe(CN)_5NO^{3-}$ (2.8×10^2 s^{-1}) is independent of the nature of the reducing radical and pH (4.6–8.5); k_{obsd} increases with increasing $[H^+]$ ($>10^{-4}$ M) or $[CN^-]$. The relative concentrations of the two reduced species depend markedly on pH and $[CN^-]$, but not radiation dose. The reduced species are sensitive to O_2 generating $Fe(CN)_5NO^{2-}$, $Fe(CN)_4NO(OH)^{2-}$, and polymeric species. In solutions containing *tert*-butyl alcohol as the OH radical scavenger, $Fe(CN)_5NO^{3-}$ reacts rapidly with $\cdot CH_2C(CH_3)_2OH$ ($k = 2.5 \times 10^9$ M^{-1}) to form a red (λ_{max} 475 nm, ϵ_{max} 5.1×10^3 M^{-1} cm^{-1}), air-insensitive, moderately stable alkylnitroso complex, $Fe(CN)_5N(O)CH_2C(CH_3)_2OH^{3-}$, the IR spectrum of which has been obtained in a KBr matrix.

Introduction

For more than a decade, the one-electron reduction of pentacyanonitrosylferrate(II) ion, $Fe(CN)_5NO^{2-}$ (nitroprusside ion), has been intensely investigated. Yet, many of the early studies were either incomplete or erroneous because of unexpected thermal or photochemical processes which resulted only in a partial resolution of the primary and secondary reactions. Recently ESR[3,4] and electrochemical[5] studies of solutions or solids containing the reduced species have been directed toward the resolution of questions concerning the electronic structure and reactivity of those species.

Our general interest in the reduction of metal nitrosyls[6,7] and our specific interest in the use of simple iron nitrosyls as models for the more complex nitrosylmyoglobin which imparts a desirable color to cured meats have led to this detailed investigation of the one-electron reduction of $Fe(CN)_5NO^{2-}$ in aqueous solution using radiation chemical techniques.[8] Continuous and pulse radiolyses, the latter with optical absorption and kinetic conductivity detection, have been used to obtain the absorption spectra of the reduced species and their kinetic parameters. The kinetic conductivity technique[9-11] is particularly useful for reactions involving protonation, weakly absorbing materials, and, as with $Fe(CN)_5NO^{2-}$, photosensitive compounds.[12] We report herein the rate constants for the reduction of $Fe(CN)_5NO^{2-}$ by a variety of reducing radicals, the absorption spectra of the reduced species, the kinetics of the loss of CN^- from the initial reduced species, and the reaction of the reduced species with the radical derived from the reaction of OH radicals with *tert*-butyl alcohol.

Experimental Section

Materials. Sodium pentacyanonitrosylferrate(II), $Na[Fe(CN)_5NO]\cdot 2H_2O$, was obtained from Mallinckrodt or Alfa-Ventron and recrystallized from warm water in the dark. Distilled water was further purified by passage through a Millipore purification train. Nitrogen and argon were scrubbed with 1 M basic pyrogallol or Cr^{2+} (followed by 0.1 M NaCl) in all-glass flow system. All other reagents were of the highest quality available and were used without further purification. Solutions were buffered with $HClO_4$, phosphate, or NaOH.

Radiation Techniques. Pulse radiolyses with optical absorption detection were performed using the apparatus (time resolution ~0.5 μs) at the U.S. Army Natick Research and Development Command.[12] The radiation dose per pulse was established by the use of SCN^- dosimetry.[13] Pulse radiolyses with kinetic conductivity detection were performed using the apparatus (time resolution ~3 μs) at the Hahn-Meitner Institut[9] which allows the observation of very small changes in conductivity corresponding to changes in ionic concentrations as low as 10^{-7} M. Continuous radiolyses were performed in a ^{60}Co γ-ray source with a dose rate of ~13 krd min^{-1}. The exact doses delivered to the solutions were determined using the Fricke dosimeter.

In the kinetic conductivity technique, the formation or decay of charged species in the pulsed solution results in a signal voltage, ΔV, which can be followed as a function of time oscilloscopically. The value of ΔV depends on the net change in concentration, ΔC, and specific conductivity, Λ, of the ions involved.[14] For quantitative analysis, the signal voltage obtained for an unknown system, ΔV_x, is compared with that of a known reference system, ΔV_r, where

$$\frac{\Delta V_x}{\Delta V_r} = \frac{\Delta C_x \Lambda_x}{\Delta C_r \Lambda_r}$$

The concentration change can be related directly to the G values (number of molecules or ions formed or destroyed per 100 eV of energy absorbed by the solution) of formation or loss of the unknown or reference. A suitable reference system is provided by the tetranitromethane dosimeter[9] which consists of an N_2O-saturated (2.5×10^{-2} M) slightly acidic aqueous solution of 1×10^{-3} M $C(NO_2)_4$ and 0.1 M 2-propanol. Irradiation of this solution results in the generation of $C(NO_2)_3^-$ and H_{aq}^+, the yield ($G_r = 5.1$)[9,15] and specific conductivities ($\Lambda_r = \Lambda(C(NO_2)_3^- + H_{aq}^+) = 45 + 315 = 360\ \Omega^{-1}\ cm^2$)[9] of which are known. The measured signal voltage, therefore, permits the calculation of $G_x\Lambda_x$ or $\Delta C_x \Lambda_x$ for the unknown system.

Generation of the Reducing Radicals. The radiolysis of water and aqueous solutions generates e_{aq}^-, OH radicals, and H atoms according to the overall reaction $H_2O \rightsquigarrow e_{aq}^-$ (2.8), OH (2.8), H (0.55) where the numbers in parentheses represent the G values of the species. By the use of selected scavengers, a particular reactive radical can be chosen to be the principal reactant in the solution. Thus, in the presence of *tert*-butyl alcohol, the OH radicals are effectively scavenged: $OH + (CH_3)_3COH \rightarrow \cdot CH_2(CH_3)_2OH + H_2O$ ($k = 5.2 \times 10^8$ M^{-1} s^{-1});[16] the resultant radical's weak optical absorption[12] below 280 nm can easily be taken into account when transient absorption spectra are determined. In N_2O-saturated solution, e_{aq}^- is efficiently scavenged: $e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^-$ ($k = 8.7 \times 10^9$ M^{-1} s^{-1}).[17] In acidic solution e_{aq}^- is converted to H atoms: $e_{aq}^- + H^+ \rightarrow H$ ($k = 2.2 \times 10^{10}$ M^{-1} s^{-1}).[17] The reducing radicals, CO_2^-, $\cdot CH_2OH$, and $(CH_3)_2\dot{C}OH$ can be generated conveniently from solutions containing formate, methanol, or 2-propanol: $OH/H + HCO_2^- \rightarrow CO_2^- + H_2O/H_2$ ($k = 2.5 \times 10^9/5.0 \times 10^7$ M^{-1} s^{-1});[16,18] $OH/H + CH_3OH \rightarrow \cdot CH_2OH + H_2O/H_2$ ($k = 7.6 \times 10^8/1.6 \times 10^6$ M^{-1});[16,18] $OH/H + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O/H_2$ ($k = 1.3 \times 10^9/5.0 \times 10^7$ M^{-1} s^{-1}).[16,18] The reaction of OH and H with 2-propanol also generates the β radical, $\cdot CH_2C(CH_3)HOH$, in ~15% yield;[15] this radical is a much weaker reducing agent than is $(CH_3)_2\dot{C}H$.[19] Thus, by the judicious choice of scavengers, selected reactive radicals of known stoichiometry can be generated.

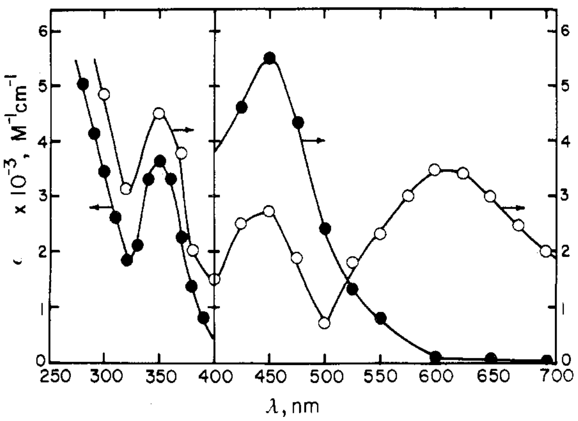

Figure 1. Absorption spectra obtained from the reaction of CO_2^- radicals with 5 × 10^{-4} M $Fe(CN)_5NO^{2-}$ in N_2O-saturated solution containing 0.5 M $NaHCO_2$ and 1 mM phosphate buffer at pH 7.0. Spectra were corrected for loss of substrate in the pulse and were recorded at 20 μs (●) and 10 s (○) after the pulse. The same initial transient spectrum is also produced upon reaction of $Fe(CN)_5NO^{2-}$ with $(CH_3)_2\dot{C}OH$ at pH 1–8.5 and e_{aq}^- at pH 7.0.

Table I. Rate Constants for the Reduction of $Fe(CN)_5NO^{2-}$

Radical	k, M^{-1} s^{-1}	Radical	k, M^{-1} s^{-1}
e_{aq}^{-} [a]	1.0 × 10^{10}	CO_2^- [c]	4.0 × 10^8
	(2.4 × 10^{10})[f]		(3.7 × 10^8)[h]
	(2.2 × 10^{10})[g]	$(CH_3)_2\dot{C}OH$[d]	2.9 × 10^9
H[b]	7 × 10^7	$\cdot CH_2OH$[e]	6.0 × 10^8

[a] 5 × 10^{-4} M $Fe(CN)_5NO^{2-}$, 0.5 M *tert*-butyl alcohol, 0.13 M phosphate buffer, pH 8.5, Ar purged. [b] 4 × 10^{-4} M $Fe(CN)_5NO^{2-}$, pH 4.6, N_2O saturated. [c] 5 × 10^{-4} M $Fe(CN)_5NO^{2-}$, 0.1 M HCO_2^-, 0.01 M phosphate buffer, pH 7.0, N_2O saturated. [d] 5 × 10^{-4} M $Fe(CN)_5NO^{2-}$, 0.5 M 2-propanol, 0.1 M phosphate buffer, pH 7.0, N_2O saturated. [e] 5 × 10^{-4} M $Fe(CN)_5NO^{2-}$, 0.5 M methanol, 0.13 M phosphate buffer, pH 8.5, N_2O saturated. [f] M. Anbar and E. J. Hart, *Adv. Chem. Ser.*, No. 81, 79 (1968); concentrations unspecified, pH 10.5, $\mu = 1 \times 10^{-4}$ M (?). It should be noted that $Fe(CN)_5NO^{2-}$ is subject to extensive hydrolysis at pH 10.5 so that the exact nature of the e_{aq}^- scavenger is in doubt. [g] Reference 8; conditions unspecified. [h] Reference 8; 2 × 10^{-4} M $Fe(CN)_5NO^{2-}$, 0.02 M HCO_2^-, unbuffered, neutral, N_2C saturated.

Table II. Spectral Characteristics

Compd	Formalism	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
$Fe(CN)_5NO^{2-}$ [a]	[Fe^{II}-NO^+]	480	~8
		394	25
		330 sh	40
$Fe(CN)_5NO^{3-}$ [b]	[Fe^{II}-$\dot{N}O$]	430	550
		345	3500
$Fe(CN)_4NO^{2-}$ [b]	[Fe^{I}-NO^+]	615	380
		430	100
		350	300
$Fe(CN)_5N(O)R^{3-}$ [b,c]	[Fe^{II}-N(O)R]	476	5100
		250	8900

[a] Reference 31. [b] This work. [c] $R = CH_2C(CH_3)_2OH$.

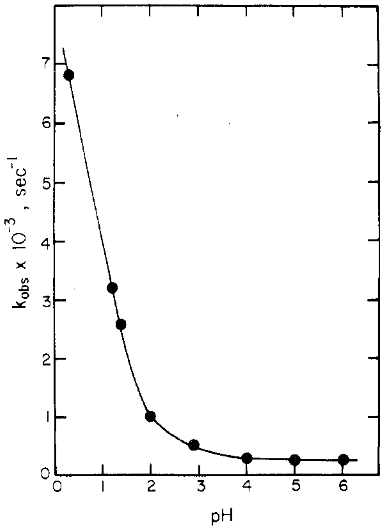

Figure 2. Dependence of k_{obsd} on pH in the pulse radiolysis of N_2O-saturated solution of 5 × 10^{-4} M $Fe(CN)_5NO^{2-}$ in 0.5 M 2-propanol; λ 350 nm, dose/pulse = 4 krd.

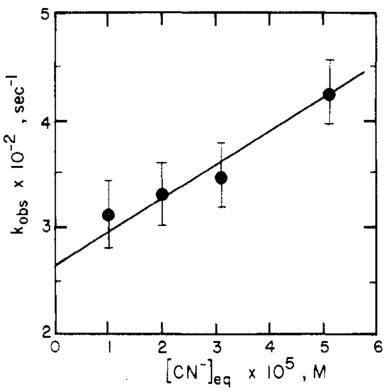

Figure 3. Dependence of k_{obsd} on $[CN^-]_{eq}$ in the pulse radiolysis of N_2O-saturated solution of 5 × 10^{-4} M $Fe(CN)_5NO^{2-}$, 0.1 M HCO_2^-, 0.1 M phosphate buffer at pH 6.7; λ 350 nm, dose/pulse = 4 krd. $[CN^-]_{eq} = [CN^-]_0(1 + [H^+]/K_a)^{-1}$; $K_a = 4.9 \times 10^{-10}$.

Analyses. Ion-exchange separation of the products of continuous radiolysis was accomplished on Sephadex-A25 DEAE or QAE anion-exchange resin (Pharmacia). Neutral solutions cf NaCl or KBr served as eluents. The charge of the products was deduced from their behavior on the ion-exchange column relative to that of $Fe(CN)_5NO^{2-}$; identification of the products was made on the basis of their UV–vis absorption spectra. Free NO_2^- was analyzed spectrophotmetrically using the method of Shin.[20] Cary 14 and 15 and Beckman IR9 spectrophotometers were used.

Results and Discussion

Free-Radical Reduction. The reaction of the one-electron reducing radicals with $Fe(CN)_5NO^{2-}$ yields the transient absorption spectrum shown in Figure 1 (closed circles; λ_{max} 345 and 440 nm; ϵ_{max} 3.5 × 10^3 and 5.5 × 10^2 M^{-1} cm^{-1}, respectively). From the pseudo-first-order kinetics of the formation of this spectrum or the decay of e_{aq}^-, the rate constants for reaction 1 are evaluated and presented in Table

$$\mathrm{Fe(CN)_5NO^{2-} + Red \rightarrow Fe(CN)_5NO^{3-} + Ox} \qquad (1)$$

I. This transient absorption is attributed to $Fe(CN)_5NO^{3-}$ where the added electron is localized mainly on the π^*(NO) orbital[3,21] (Table II). The transient spectrum is independent of pH (1–8.5); experiments in more alkaline solution were not conducted due to the base hydrolysis of $Fe(CN)_5NO^{2-}$.[22] There is no evidence that this initial reduced species is in an electronically excited state.[23]

The initial transient absorption decays via first-order kinetics to yield a secondary spectrum (Figure 1; open circles) which is stable for at least several hours in the absence of light and air. The relative intensities of the bands at 345, 440, and 615 nm remaining after the decay are dependent on pH, the concentration of CN^- initially present, but not the radiation dose delivered by the pulse.

The observed rate constant, k_{obsd}, for the decay of the initial transient is independent of the nature of the reducing radical; in the absence of initially present CN^-, k_{obsd} = 2.8 (±0.4) × 10^2 s^{-1} and is independent of pH in the range 4.6–8.5. However, k_{obsd} increases markedly in more acidic medium (Figure 2) and is a linear function of the equilibrium con-

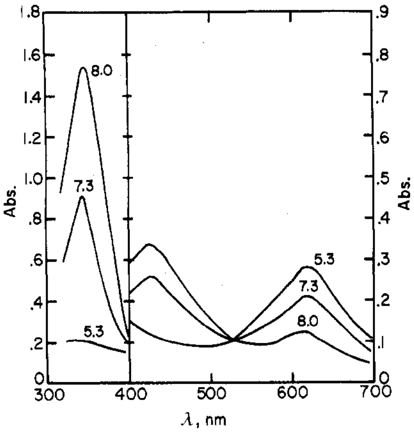

Figure 4. Absorption spectra from the continuous radiolysis (125.3 krd) of 2×10^{-3} M $Fe(CN)_5NO^{2-}$ in N_2O-saturated solution containing 0.1 M HCO_2^- and 0.01 M phosphate buffer at the pH values shown; dose rate 7.7×10^{17} eV L^{-1} min^{-1}.

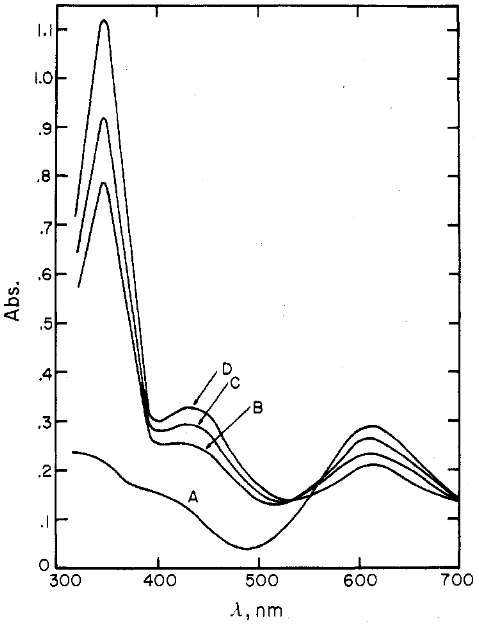

Figure 5. Absorption spectra from the continuous radiolysis (146.0 krd) of 2×10^{-3} M $Fe(CN)_5NO^{2-}$ in N_2O-saturated solution containing 0.1 M HCO_2^- and 0.1 M phosphate buffer at the pH 5.3–5.6. Concentration of added NaCN: A, none; B, 0.0075 M; C, 0.0085 M; D, 0.01 M. Dose rate = 7.7×10^{17} eV L^{-1} min^{-1}.

centration of CN^- at a fixed pH (Figure 3).

Figure 4 shows that the same spectra are obtained from the continuous radiolysis of a N_2O-saturated solution of 2×10^{-3} M $Fe(CN)_5NO^{2-}$ containing 0.1 M HCO_2^- as from the pulse radiolysis (Figure 1). Solutions at pH 5.3, 7.3, and 8.0 are blue, green, and brown, respectively, with a single isosbestic point at 530 nm. From a knowledge of the molar absorptivity of the initially produced brown $Fe(CN)_5NO^{3-}$ and the fact that it is almost totally converted to the blue product at pH <5, an estimate of the molar absorptivity of this product can be made from both pulse and continuous radiolysis data: ϵ_{615} 380, ϵ_{430} 100, and ϵ_{350} 300 M^{-1} cm^{-1}.

At constant pH (5.4 ± 0.2) established with 0.1 M phosphate, the concentration of added CN^- was varied prior to continuous radiolysis. Figure 5 shows the spectra of the products under these conditions.

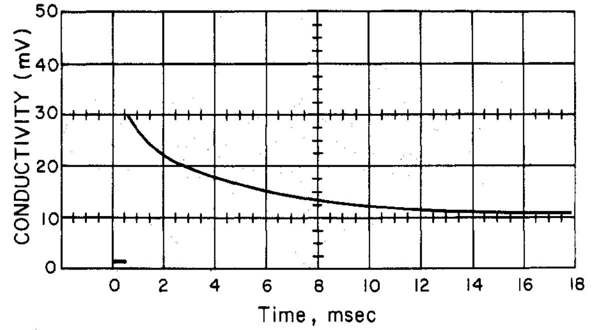

Figure 6. Change in conductivity signal upon the pulse radiolysis of 1×10^{-3} M $Fe(CN)_5NO^{2-}$ in 0.2 M *tert*-butyl alcohol at pH 4.6 (Ar purged), dose/pulse ~ 1 krd.

Figure 6 shows a typical oscilloscope trace obtained from kinetic conductivity pulse radiolysis experiments on 1×10^{-3} M $Fe(CN)_5NO^{2-}$ in 0.2 M *tert*-butyl alcohol at pH 4.6 (Ar purged). The initial rapid increase in conductivity is an immediate consequence of the primary radiolysis in which H_{aq}^+ is generated and the replacement of $Fe(CN)_5NO^{2-}$ by $Fe(CN)_5NO^{3-}$ via the fast reaction with e_{aq}^-. If $Fe(CN)_5NO^{3-}$ were rapidly to protonate to give $Fe(CN)_5NOH^{2-}$ as proposed by Van Voorst and Hemmerich,[21] the initial increase in conductivity would not be observed. The subsequent decrease in conductivity to a new and stable value occurs via first-order kinetics ($k = 2.6 \times 10^2$ s^{-1}). The final value of the conductivity is higher than the prepulse value.

Detachment of CN^-. The spectral changes and their dependence on pH and $[CN^-]$, the dependence of k_{obsd} on $[CN^-]$, and the conductivity results are consistent with equilibria involving the reversible loss of CN^- and its subsequent protonation

$$Fe(CN)_5NO^{3-} \rightleftarrows Fe(CN)_4NO^{2-} + CN^- \quad (2)$$

$$CN^- + H_{aq}^+ \rightleftarrows HCN \quad (3)$$

Inasmuch as reaction 3 is the rapid protonation of a strong base and $K_3 = 2.0 \times 10^9$, k_{obsd} represents reaction 2.

The species absorbing at 615 nm is identified as $Fe(CN)_4NO^{2-}$ (Table II) which has been generated in liquid NH_3 and aqueous and aprotic solvents.[4,5b,21,24] Between 300 and 700 nm, this species does not exhibit absorption bands that are more intense than that at 615 nm. EPR measurements and SCCC–MO calculations have indicated[4,21,24b] that the species contains the $[Fe^I\text{–}NO^+]$ entity with the electron localized mainly on the iron d_{z^2} orbital.

Values of k_2 estimated from cyclic voltammetric[5b] and polarographic[25] data are within an order of magnitude of the value of k_{obsd} reported here.

The dependence of the concentrations of $Fe(CN)_5NO^{3-}$ and $Fe(CN)_4NO^{2-}$ at equilibrium on the concentration of added CN^- at constant pH allows the evaluation of K_2. In Table III are the results of pulse radiolysis experiments at pH 6.7 and 7.9 from which is obtained $K_2 = 6.8\ (\pm 1.9) \times 10^{-5}$. From this value of K_2 and the identification of k_{obsd} at pH 4.6–8.5 as k_2, the value of $k_{-2} = 4 \times 10^6$ M^{-1} s^{-1} is obtained.

If the concentration of CN^- free in solution is greater than that of $Fe(CN)_4NO^{2-}$ as it is generated in reaction 2, the reverse reaction will be pseudo first order in CN^- and the rate expression for the decay of $Fe(CN)_5NO^{3-}$ reduces[26] to $-d[Fe(CN)_5NO^{3-}]/dt = (k_2 + k_{-2}[CN^-])[Fe(CN)_5NO^{3-}]$ where $[CN^-]$ is fixed by the pH of the solution. The intercept of the line in Figure 3 gives k_2 (2.7×10^2 s^{-1}) and the slope k_{-2} (4×10^6 M^{-1} s^{-1}).

The small value of K_2 for the reversible loss of CN^-, presumably from the trans position, is due to the strongly basic nature of CN^-. However, the weakening of the trans Fe–CN bond can be envisioned as occurring from repulsion between the density of the added electron, which is partially localized (~25%)[3,21,24] on the metal $d_{z^2}\text{–}\sigma^*$ antibonding orbital, and the σ-bonding orbital from the donor CN^-. Thus, loss of CN^- is

Table III. Evaluation of the Ligand Labilization Equilibrium Constant[a]

$[Fe(CN)_5NO^{3-}]_0$,[b] M	$[CN^-]_0$, M	$[CN^-]_{eq}$,[c] M	$[Fe(CN)_5NO^{3-}]_{eq}$,[d] M	$[Fe(CN)_4NO^{2-}]_{eq}$,[e] M	K_{eq}
		pH 6.7; $[H^+] = 2.0 \times 10^{-7}$ M			
8.6×10^{-6}	0	8×10^{-6} [f]	9×10^{-7}	8×10^{-6}	7×10^{-5}
9.0×10^{-6}	4.2×10^{-3}	1.0×10^{-5}	1.6×10^{-6}	7.4×10^{-6}	4.6×10^{-5}
9.0×10^{-6}	8.4×10^{-3}	2.0×10^{-5}	1.7×10^{-6}	7.3×10^{-6}	8.6×10^{-5}
8.6×10^{-6}	1.3×10^{-2}	3.1×10^{-5}	2.3×10^{-6}	6.3×10^{-6}	8.5×10^{-5}
8.0×10^{-6}	1.7×10^{-2}	4.2×10^{-5}	3.6×10^{-6}	4.4×10^{-6}	5.1×10^{-5}
8.6×10^{-6}	2.1×10^{-2}	5.1×10^{-5}	4.1×10^{-6}	4.5×10^{-6}	5.6×10^{-5}
		pH 7.9; $[H^+] = 1.3 \times 10^{-8}$ M			
6.6×10^{-6}	0	6×10^{-6} [f]	7×10^{-7}	6×10^{-6}	5×10^{-5}
6.6×10^{-6}	1.0×10^{-3}	3.6×10^{-5}	2.4×10^{-6}	4.2×10^{-6}	6.3×10^{-5}
6.6×10^{-6}	2.1×10^{-3}	7.6×10^{-5}	2.9×10^{-6}	3.7×10^{-6}	9.7×10^{-5}
6.6×10^{-6}	4.2×10^{-3}	1.5×10^{-4}	4.1×10^{-6}	2.5×10^{-6}	9.1×10^{-5}
6.6×10^{-6}	8.3×10^{-3}	3.0×10^{-4}	5.6×10^{-6}	1.0×10^{-6}	5.4×10^{-5}
		Av 6.8×10^{-5}; Std Dev 1.9×10^{-5}			

[a] From pulse radiolysis data; λ 350 nm, optical path 2 cm, dose/pulse = 4 krd, $[Fe(CN)_5NO^{2-}] = 5 \times 10^{-4}$ M, [phosphate buffer] = 0.1 M, $[HCO_2^-] = 0.1$ M, N_2O saturated. [b] From the initial transient absorption taking ϵ_{350} 3.5×10^3 M^{-1} cm^{-1}. [c] $[CN^-]_{eq} = [CN^-]_0(1 + [H^+]/K_a)^{-1}$; $K_a = 4.9 \times 10^{-10}$. [d] From the transient absorption at equilibrium, λ 350 nm. [e] $[Fe(CN)_4NO^{2-}]_{eq} = [Fe(CN)_5NO^{3-}]_0 - [Fe(CN)_5NO^{3-}]_{eq}$. [f] $[CN^-]_{eq} = [Fe(CN)_4NO^{2-}]_{eq}$.

accompanied by intramolecular electron transfer: $[Fe^{II}\text{–}\dot{N}O] \rightarrow [Fe^{I}\text{–}NO^+]$. The increase in k_{obsd} in acidic solution is consistent with the protonation of the leaving CN^- group prior to or during labilization. It should be noted that $Fe(CN)_6^{3-}$ is protonated at pH ~1.[27]

In aqueous solution, loss of CN^- from $Fe(CN)_5NO^{3-}$ is apparently not accompanied by coordination of H_2O. A number of observations support this contention: (1) the band at ~610 nm assigned to $Fe(CN)_4NO^{2-}$ is the same in aprotic solvents (CH_2Cl_2,[5b] CH_3CN,[5b,24a] and DMF[21,24b]) and aqueous medium; (2) the ESR spectrum in DMF[21] is similar to that of a single crystal[4] of a salt of $Fe(CN)_4NO^{2-}$ shown by x-ray diffraction to be pentacoordinate.[24b] The change in coordination around the metal center from six to five is accompanied by transfer of the odd electron on the NO ligand to the metal-localized d_{z^2} orbital yielding a species where the iron is formally in a +1 oxidation state. This process may also be viewed as an example of the amphoteric nature of coordinated nitrosyl.[28]

The labilization of the ligand trans to the nitrosyl may be a general phenomenon resulting from the one-electron reduction of complexes having a formal ground-state configuration $M^{II}\text{–}NO^+$. We have found[29] that the one-electron reduction of $Ru(NH_3)_5NO^{3+}$ results in the catalyzed formation of *trans*-$Ru(NH_3)_4NO(OH)^{2+}$. On the other hand, the one-electron reduction product of *cis*-$Ru(bpy)_2NO(A)$ complexes (where A = N_3^-, Cl^-, NO_2^-, NH_3^-, py, CH_3CN)[30] yields products in which the added electron is localized mainly on the nitrosyl ligand (as in the case of $Fe(CN)_5NO^{3-}$). However, the geometrical and electronic constraints imposed by π-donor bidentate bpy coordinated trans to the nitrosyl diminish the possibility of ligand labilization.

Oxidation of the Reduced Species. The addition of O_2 to an irradiated $Fe(CN)_5NO^{2-}$ solution (~50% reduction) results in the loss of the absorption bands of the reduced species and the regeneration of the spectra of the starting solution. Anion-exchange chromatography of the oxidized solution resulted in the removal of a brown product upon elution with 0.75 M KBr at pH 7.0; the absorption spectrum of this product was the same as that of $Fe(CN)_5NO^{2-}$ from 300 to 700 nm.[31] The IR spectrum in a KBr matrix of the solid obtained from the rotoevaporation of the oxidation product shows the strong ν_{NO} band at 1945 cm^{-1} and a shoulder at 1910 cm^{-1}, the intensity of which depends upon the pH of the original solution and the extent of loss of volatile HCN during the O_2-saturation procedure. By analogy to $Ru(NH_3)_5NO^{3+}$ (ν_{NO} 1910 cm^{-1})[33] and *trans*-$Ru(NH_3)_4NO(OH)^{2+}$ (ν_{NO} 1848 cm^{-1}),[34] the shoulder at 1910 cm^{-1} is attributed to $Fe(CN)_4NO(OH)^{2-}$. Despite the overall negative charge of the complex, the pK_a of the conjugate acid is expected to be below 7 (pK_a of $RuCl_4NO(OH_2)^-$ is ~6).[35] This attribution would explain the elution of only one brown band upon anion exchange at pH 7. Assuming the UV-vis spectra of $Fe(CN)_5NO^{2-}$ and $Fe(CN)_4NO(OH)^{2-}$ to be very similar, it is estimated that 75–80% of the original substrate can be accounted for. Small amounts of more highly charged products, which are presumably polymeric materials, and free NO_2^- were also separated.

Pulse radiolysis experiments showed that the lifetime of $Fe(CN)_5NO^{3-}$ was not affected by the presence of 4×10^{-5} M O_2; CN^- detachment was the only process observed. From this result we conclude that $k(Fe(CN)_5NO^{3-} + O_2) \leq 1 \times 10^6$ M^{-1} s^{-1}. This value is to be compared with $k(Ru(NH_3)_5NO^{2+} + O_2) = 7.6 \times 10^6$ M^{-1} s^{-1}.[6] When exposed to O_2, solutions at pH ~8 containing largely $Fe(CN)_5NO^{3-}$ bleached almost instantaneously. In contrast, solutions containing primarily $Fe(CN)_4NO^{2-}$ at pH ≤5 bleached slowly (~30 s) when bubbled with O_2. In CH_2Cl_2 and CH_3CN solutions, the same insensitivity of $Fe(CN)_4NO^{2-}$ toward O_2 was observed,[5b] which is surprising in light of the assumed $Fe^{I}\text{–}NO^+$ structure of that species. The reaction of $Fe(CN)_5NO^{3-}$ with O_2 is probably electron transfer in nature; reaction 4 coupled with reactions

$$Fe(CN)_5NO^{3-} + O_2 \rightarrow Fe(CN)_5NO^{2-} + O_2^- \qquad (4)$$

2 and 3 could be the mode of disappearance of $Fe(CN)_4NO^{2-}$. It follows from these observations that $k(Fe(CN)_4NO^{2-} + O_2) << k(Fe(CN)_5NO^{3-} + O_2)$. The $Fe(CN)_4NO^{2-} + O_2$ reaction may occur via electron transfer or via initial addition of O_2 to the vacant sixth coordination site of the square-pyramidal $Fe(CN)_4NO^{2-}$ complex; the comparable addition of O_2 to $Co(CN)_5NO^{3-}$ ($k > 10^5$ M^{-1} s^{-1})[36] and $Rh(NH_3)_4^{2+}$ ($k = 3.1 \times 10^8$ M^{-1} s^{-1})[37] demonstrates the reactivity of coordinatively unsaturated low-spin d^7 complexes.

Reaction of Reduced Species with Radicals. The continuous radiolysis of Ar-purged solutions of 2×10^{-3} M $Fe(CN)_5NO^{2-}$ in 0.5 M *tert*-butyl alcohol at pH 7.2 yielded the spectrum shown in Figure 7 which is to be compared with those shown in Figure 4 for irradiation of N_2O-saturated HCO_2^- solutions. In the former case, e_{aq}^- and H atoms are the reducing radicals with OH scavenged by the alcohol to yield $\cdot CH_2C(CH_3)_2OH$ radicals; in the latter case, the only reactive radical present is CO_2^-. Pulse radiolysis showed that the decay of the 350-nm band of $Fe(CN)_5NO^{3-}$ paralleled the rise of the 475-nm absorbance of the product with second-order kinetics (Figure

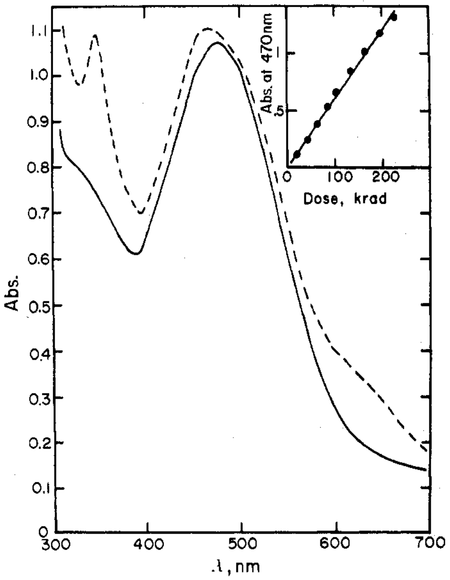

Figure 7. Absorption spectrum of the solution from the 50% reduction of 2×10^{-3} M $Fe(CN)_5NO^{2-}$ in 0.5 M *tert*-butyl alcohol at pH 7.2 (0.01 M phosphate buffer; Ar purged) (---) and of the same solution upon saturation with O_2 after irradiation (—); radiation dose rate 12.4 krd min^{-1}. Insert: absorbance at 470 nm as a function of delivered radiation dose at pH 8.4.

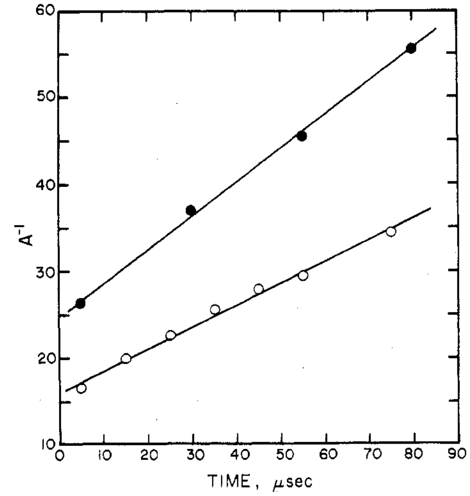

Figure 8. Second-order plot of the formation of 475-nm absorption (○) and decay of 350-nm absorption (●) from the pulse radiolysis of an Ar-purged solution of 5×10^{-4} M $Fe(CN)_5NO^{2-}$ in 0.5 M *tert*-butyl alcohol at pH 4.6; dose/pulse = 20 krd; optical path 2 cm; taking ϵ_{350} 3.5×10^3 M^{-1} cm^{-1} and ϵ_{475} 5.1×10^3 M^{-1} cm^{-1}, $k_{350} = k_{475} = 2.5 \times 10^9$ M^{-1} s^{-1}.

8); the usual first-order decay of the unreacted $Fe(CN)_5NO^{3-}$ described by reaction 2 occurred subsequently. By analogy to the formation of an alkylnitroso complex from the reaction between $Ru(NH_3)_5NO^{2+}$ and $\cdot CH_2C(CH_3)_2OH$,[7] the formation of the red product here is attributed to reaction 5 for

$$Fe(CN)_5NO^{3-} + \cdot CH_2C(CH_3)_2OH \rightarrow Fe(CN)_5N(O)CH_2C(CH_3)_2OH^{3-} \tag{5}$$

$$2 \cdot CH_2C(CH_3)_2OH \rightarrow \text{products} \tag{6}$$

which $k_5 = 2.5 \times 10^9$ M^{-1} s^{-1}. In comparison, $k_6 = 7.0 \times 10^8$ M^{-1} s^{-1}.[12] Approximately 50% of the $Fe(CN)_5NO^{3-}$ initially generated reacts via reaction 5 and the remainder establishes the equilibrium of reaction 2. Under pulse conditions, this yield is independent of pH (4.6–8.8). In the kinetic conductivity experiments, reaction 5 is barely detected because of the lack of overall net change in charge; the differences in the specific conductivities of the 3– charged ions is quite small.

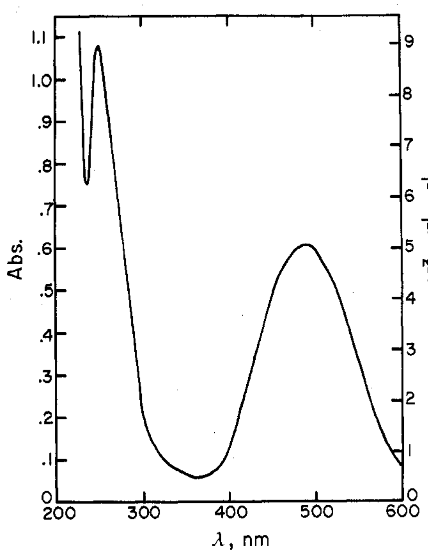

Figure 9. Absorption spectrum of $Fe(CN)_5N(O)CH_2C(CH_3)_2OH^{3-}$.

Figure 7 shows that upon continuous irradiation at pH 7, $Fe(CN)_5NO^{3-}$ (λ_{max} 345 nm) and $Fe(CN)_4NO^{2-}$ (λ_{max} 615 nm) are present in addition to the red adduct. The insert to Figure 7 illustrates that at pH 8.4, where the reduction product is largely $Fe(CN)_5NO^{3-}$, there is a linear production of adduct in an amount equal to ~50% of the $Fe(CN)_5NO^{3-}$ generated. At pH <8, the amount of adduct formed in continuous radiolysis diminishes appreciably as pH is lowered indicating that $Fe(CN)_4NO^{2-}$ does not lead to the formation of the adduct. Pulse radiolysis experiments with N_2O-saturated solutions containing 1×10^{-3} M $Fe(CN)_5NO^{2-}$ and 0.5 M *tert*-butyl alcohol gave no evidence for a direct reaction between the $\cdot CH_2C(CH_3)_2OH$ radical and $Fe(CN)_5NO^{2-}$. Figure 7 also shows that saturation of the irradiated solution with O_2 results in the removal of the reduced species but not the red adduct which is obviously air insensitive.

Attempts to isolate the red product as the Na^+, Cs^+, Et_4N^+, or Ba^{2+} salts were frustrated by the thermal instability or high solubility of the complex in a number of solvents. As expected for an iron(II)–cyano complex,[38] its aqueous solutions are photosensitive. The red adduct, however, was separated from the reaction mixture by anion exchange and elution with 0.3 M KBr. Figure 9 shows the absorption spectrum of $Fe(CN)_5N(O)CH_2C(CH_3)_2OH^{3-}$ from the ion-exchange separation. Molar absorptivities were estimated from the quantitative conversion of the adduct to $Fe(CN)_6^{4-}$ by treatment with excess CN^- at pH 10.

The absorption spectrum shown in Figure 9 is very similar to those of the short-lived complexes generated from the reaction in alkaline medium of $Fe(CN)_5NO^{2-}$ with organic compounds, such as ketones, containing acidic α protons.[39,40] The adduct formed in this study is the alcohol analogue which is also unstable toward base hydrolysis. However, inasmuch as there is no requirement of the presence of base in the radiolytic synthesis, alkylnitroso derivatives can be generated and stabilized under more favorable conditions.

Rotoevaporation to dryness of the ion-exchanged solution permitted the IR spectrum of the alkylnitroso product to be obtained in a KBr matrix. The spectrum, shown in Figure 10, is supportive of the formulation of the complex as $K_3[Fe(CN)_5N(O)CH_2C(CH_3)_2OH]\cdot H_2O$. There is no evidence for the band at 1945 cm^{-1} characteristic of the nitrosyl of the starting material.[32] The intense band at 2080 cm^{-1} is assigned to ν_{CN} and is characteristic of $Fe^{II}(CN)_5L$ complexes where L is not a strong π-acceptor ligand.[41] The bands at 3500

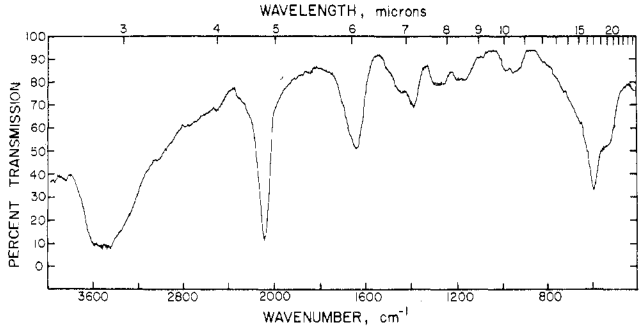

Figure 10. Infrared spectrum of $Fe(CN)_5N(O)CH_2C(CH_3)_2OH^{3-}$ in a KBr matrix.

and 1631 cm^{-1} may be assigned to lattice H_2O; the band at 3500 cm^{-1} would obscure the O–H alcohol mode expected in this region. Bands at 590 and 525 cm^{-1} are attributed to $\nu_{\text{Fe-CN}}$.[41] Between 1575 and 1150 cm^{-1}, several weak bands are resolved which occur in regions characteristic of both the fingerprint for the alkyl backbone and ν_{NO} of the nitroso moiety.[43]

The reaction of $Fe(CN)_5NO^{3-}$ with free radicals appears

$$Fe(CN)_5NO^{3-} + R\cdot \rightarrow Fe(CN)_5N(O)R^{3-} \tag{7}$$

to be a general synthetic route to iron alkylnitroso complexes and their derivatives. Further details about reaction 7 and the analogous reaction of $Ru(NH_3)_5NO^{2+}$ will be presented in a separate publication.[44]

Registry No. $Fe(CN)_5NO^{2-}$, 15078-28-1; $Fe(CN)_5NO^{3-}$, 14636-58-9; $Fe(CN)_4NO^{2-}$, 55188-49-3; $Fe(CN)_5N(O)CH_2C(CH_3)_2OH^{3-}$, 63231-44-7; CN^-, 57-12-5.

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Kinetics and Equilibria for Carbon Monoxide and Benzyl Isocyanide Binding to Ferrous Tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine

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Syntheses, visible spectra, and NMR are reported for low-spin iron(II) complexes of the macrocyclic ligand TAAB ($[FeTAAB(L)_2](PF_6)_2$, L = methylimidazole, pyridine, acetonitrile, and benzyl isocyanide, and $[FeTAAB(L)(X)](PF_6)_2$, X = CO). The complexes undergo axial ligand substitution reactions via a dissociative mechanism in acetonitrile and acetone solution. Stability constants and rate constants for CO and BzlNC binding are compared with analogous data for phthalocyanine, porphyrin, and dimethylglyoxime systems. Of the heme models studied the TAAB system is the poorest at binding axial π acceptors.

Introduction

Previous work has shown that axial ligand substitution reactions of tetragonal low-spin Fe(II) complexes of macrocyclic ligands for phthalocyanine,[1-3] porphyrin,[4,5] and glyoxime[6,7] systems proceed by a dissociative mechanism. The existence of comparable data for methylimidazole, carbon monoxide, and benzyl isocyanide binding to these systems allows for a detailed comparison of the effects of a macrocyclic ligand on the stability and lability of axial ligands. In these systems, differences of the order of 10^5 in stability constant