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Kinetic Studies of the Pentacyanonitrosylferrate(2−)-Azide and -Hydroxylamine Reactions

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Reactions of pentacyanonitrosylferrate(2−), ($(NC)_5FeNO^{2-}$, nitroprusside) with hydroxylamine and azide were examined. With azide at pH 6, N_2 and N_2O are produced according to the equation $(NC)_5FeN^*O^{2-} + {}^{\ddagger}NNN^- + H_2O = (NC)_5FeH_2O^{3-} + N_2 + {}^{\ddagger}NN^*O$. The rate law for the first step, the formation of a nitrosyl–azide adduct, I, is assumed to be $d[I]/dt = k_{1a}[(NC)_5FeNO^{2-}][N_3^-]$, with $k_{1a} \approx 0.2\ M^{-1}\ sec^{-1}$ at pH 6, $T = 23°$. This adduct decomposes to give $(NC)_5FeH_2O^{3-}$ (λ_{max} 455 nm, ϵ 460 $M^{-1}\ cm^{-1}$), N_2, and N_2O; and the rate law is assumed to be $-d[I]/dt = k_{1b}[I]$; k_{1b} is approximately 0.2 sec^{-1} at pH 6, $T = 23°$. The complex $(NC)_5FeH_2O^{3-}$ dimerizes to $(NC)_{10}Fe_2^{6-}$ (λ_{max} 395 nm, ϵ 940 $M^{-1}\ cm^{-1}$). In excess azide the dimer reacts to form $(NC)_5FeN_3^{4-}$ (λ_{max} 440 nm, ϵ 1400 $M^{-1}\ cm^{-1}$); the rate law is $d[(NC)_5FeN_3^{4-}]/dt = k_2[(NC)_{10}Fe_2^{6-}][N_3^-]$, with $k_2 = 1.0\ (\pm 0.1) \times 10^2\ M^{-1}\ sec^{-1}$ at pH 6, $T = 23°$. $\mathcal{E}°$ for the couple $(NC)_5FeN_3^{3-} + e^- = (NC)_5FeN_3^{4-}$ is $-0.3\ (\pm 0.1)$ V and $(NC)_5FeN_3^{4-}$ is oxidized by O_2 according to the equation $d[(NC)_5FeN_3^{3-}]/dt = k_3[(NC)_5FeN_3^{4-}][O_2]$, with $k_3 = 3.0\ (\pm 0.7) \times 10^2\ M^{-1}\ sec^{-1}$ at pH 6, $T = 23°$. Hydroxylamine reacts with $(NC)_5FeNO^{2-}$ according to the equation $(NC)_5FeNO^{2-} + {}^{\ddagger}NH_2{}^*OH + OH^- = (NC)_5FeH_2O^{3-} + N^{\ddagger}N^*O + H_2O$. An intermediate, J ($\lambda_{max}$ 445 nm, ϵ 700 $M^{-1}\ cm^{-1}$), is formed, the rate law being $d[J]/dt = k_{4a}[(NC)_5FeNO^{2-}][NH_2OH][OH^-]$, with $k_{4a} = 4.5 \times 10^5\ M^{-2}\ sec^{-1}$ at 25° and $E_a = 9.5 \pm 1.0$ kcal/mol. The possibility exists that J is $(NC)_5FeN_2O^{3-}$. Subsequent reactions occurred which were not quantitatively examined. It is apparent from these studies that the stability of pentacyanoferrate(II) complexes toward oxygen oxidation is strongly dependent on the π-accepting ability of the sixth ligand.

Introduction

The reactions of bases B^n with pentacyanonitrosylferrate(2−) (nitroprusside, $(NC)_5FeNO^{2-}$) according to the general equation

$$(NC)_5FeNO^{2-} + B^n \rightleftarrows (NC)_5FeN(B)O^{-2+n}$$

where the base is normally bound to the nitrogen of the NO moiety, are well established[1] and numerous studies of the kinetics and stability of such adducts have been carried out.

Of particular interest are the reactions of the bases azide, N_3^-, and hydroxylamine, NH_2OH, with nitroprusside—both of which ultimately produce nitrous oxide, N_2O. Questions that arise concerning these reactions are as follows. (a) Are intermediates formed that have unusual ligands bound to the iron(II) center, *e.g.*, $N(N_3)O$ or N_2O? (b) What is the mechanism by which the final gaseous products are formed? *E.g.*, in the NH_2OH-$(NC)_5FeNO^{2-}$ reaction does the oxygen of the N_2O come from the NO moiety or NH_2OH?

Experimental Section

Apparatus and Measurements. Absorption spectra and some kinetic runs were carried out using a Cary Model 14 recording spectrophotometer. Temperature control for recorded spectra as well as kinetic measurements was achieved through use of a Haake constant-temperature circulator, Model F, with a Jumo contact thermometer providing thermoregulation. Temperature precision was ±0.5° for kinetic runs and ±0.2° for spectra. A Du Pont Model 310 curve resolver was used in resolving spectral envelopes. Some kinetic studies were carried out on stopped-flow apparatus: Gibson-Durrum and Durrum Model D-40 adapted to a Beckman DU spectrophotometer. Temperature control was ±0.5°.

Oxygen concentrations were determined by direct measurement on a Beckman Fieldlab oxygen analyzer calibrated with oxygen and air-saturated solutions for which the oxygen concentrations are known. A Beckman Expandomatic pH meter, calibrated against commercial standard buffers, was used in all pH measurements. The pH was assumed to represent hydrogen ion concentration. This approximation introduced no significant errors in the studies performed herein.

Quantitative and qualitative collection and sampling of gaseous products were conducted on a general-purpose vacuum line, which was equipped with a Toepler pump for manipulation of noncondensable gases. Analyses of gaseous products were conducted on a Consolidated Electrodynamics Type 21-104 cycloidal-focusing spectrometer. The resolution was sufficiently high so as to eliminate "cross talk," or peak tail overlap, in the mass ranges of interest in this study. Normal sample introduction pressures were in the 20–80-μ range. Since the introduction chamber has a volume of around 3 l., this required a sample corresponding to $(1-2) \times 10^{-5}$ mol. Qualitative observations ascertained the complete absence of peaks with m/e greater than 53 or less than 12 in all runs. Therefore, quantitative measurements were conducted by scanning m/e from 12 to 60 in the general case. Mass spectroscopic identification of the components present in samples was made by comparison of spectra with those of pure gases obtained at conditions approximating those of the samples. Background corrections were made by normalizing a known isotopic peak near the peak of interest.

Chemicals and Solutions. Sodium nitroprusside and sodium nitrite were obtained as reagent grade (Mallinckrodt) and used without further purification. Spectral properties agreed with reported values.[2] Stock solutions of sodium nitroprusside made up to 1 *M* ionic strength with sodium chloride showed a very slight change in spectral character. Hydroxylamine hydrochloride (Mallinckrodt) was recrystallized from water and dried over calcium chloride. Stock solutions were analyzed by titration with standardized iron(III) nitrate solution.[3] Sodium azide was practical grade (Mallinckrodt). After solutions were prepared and allowed to stand for *ca.* 2 hr, filtering with a fine-frit sintered-glass filtering funnel removed impurities and resulted in clear solution of greater than 99% purity. Isotopically labeled sodium nitrite, $Na^{15}NO_2$ (99.1 atom % ^{15}N), and sodium azide, $Na^{15}NN_2$, were obtained from Stohler Isotope Chemicals. Isotopically labeled potassium nitrate, $K^{15}NO_3$ (99 atom % ^{15}N), was obtained from International Chemical and Nuclear Corp. Isotopically labeled water in various degrees of ^{18}O enrichment was obtained from Bio-Rad Laboratories.

Deionized distilled water was employed in preparation of all solutions. Phosphate buffers were prepared and made up to 1 *M* ionic strength with sodium chloride. No variations in experimental results as a function of buffer capacity were observed.

Preparations. $(NC)_5FeN^{18}O^{2-}$, oxygen-18-enriched nitroprusside, was prepared *in situ*. The equilibrium

$$(NC)_5FeNO^{2-} + 2OH^- = (NC)_5FeNO_2^{4-} + H_2O$$

was used for the synthesis. The equilibrium and kinetic properties of this reaction and the aquation of $(NC)_5FeNO_2^{4-}$ are well established,[4] and by the addition of acid after an optimum time to a nitro-

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(1) J. H. Swinehart, *Coord. Chem. Rev.*, **2**, 385 (1967), and references cited therein.

(2) P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, **87**, 3340 (1965).

(3) W. C. Bray, M. E. Simpson, and A. A. MacKenzie, *J. Amer. Chem. Soc.*, **41**, 1363 (1919).

(4) J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).

prusside solution of known $[OH^-]$ the yield of $(NC)_5FeN^{18}O^{2-}$ was maximized. The detailed procedure was as follows. A 0.0598-g sample (2.00×10^{-4} mol) of $Na_2Fe(CN)_5NO\cdot 2H_2O$ was dissolved in 9.50 ml of oxygen-18-enriched water (1.90 atom % ^{18}O). One-half milliliter of 2.0 *M* NaOH was added and stirred, and after 2 min ($t_{1/2}$ = 18 sec, >98% reaction) the yellow solution was acidified to pH *ca.* 3 by rapid, dropwise addition of 0.5 *M* $HClO_4$. The solution was returned to pH *ca.* 6 by treatment with 0.1 *M* NaOH and finally buffered at pH *ca.* 8 by addition of a commercial buffer tablet (Coleman, pH 8). The appearance of the solution was consistent with that expected for a concentrated nitroprusside solution. Care must be taken that the solution does not become too strongly acidic or decomposition reactions *via* cyanide loss may occur. The resulting species, which was used immediately, had a calculated oxygen-18 enrichment of 0.93 ± 0.03%. The species $(NC)_5FeNO^{2-}$ does not undergo direct oxygen exchange.[5]

Oxygen-18-enriched hydroxylamine hydrochloride, $NH_2{}^{18}OH\cdot HCl$, was synthesized following the method of Rollefson and Oldershaw.[6] The state of oxygen-18 enrichment obtained was 0.65 (±0.05)%. The enrichment was determined by conversion of the compound to N_2O with aqueous iron(III) nitrate followed by analysis with the mass spectrometer.

Nitrogen-15-enriched hydroxylamine was prepared in the same manner as that used for preparation of $NH_2{}^{18}OH\cdot HCl$. However the scale was reduced by a factor of 10. The product, $^{15}NH_2OH\cdot HCl$, was calculated to have an enrichment of 5.1% ^{15}N, based on the potassium nitrite used in the synthesis. Mass spectral analysis, *via* oxidation to N_2O by iron(III) in acidic solution,[3] gave 5.2 (±0.2)% ^{15}N as the state of enrichment.

Nitrogen-15-enriched potassium nitrite, $K^{15}NO_2$, was prepared from isotopically enriched potassium nitrate by reduction with granulated lead, following the Heath[7] modification of the Milbauer–Vogel[8] preparation. The potassium nitrite produced retained quantitative enrichment and was 5.1% ^{15}N enriched.

The sodium salt of pentacyanoammineferrate(II), $Na_3[(NC)_5FeNH_3]\cdot 3H_2O$, was prepared following the method of Kenney, *et al.*[9] *Anal.* Calcd: C, 18.40; H, 2.78; N, 25.85. Found: C, 18.60; H, 2.74; N, 26.01.

Results

Nitroprusside–Azide Reaction. Stoichiometry and Isotopic Experiments. The reaction produces N_2 and N_2O. It was originally thought that the production of N_2 and N_2O resulted from the interaction of N_3^- with the products of the photolysis of $(NC)_5FeNO^{2-}$. However comparison of the ratio $N_2{:}N_2O = R$ with that expected from the interaction of N_3^- with the initial photolysis products of $(NC)_5FeNO^{2-}$—$(NC)_5Fe^{III}H_2O^{2-}$ and NO[10]—clearly shows that a direct thermal reaction is operative (see Discussion). Thermal and photochemical stoichiometry determinations produce the same values of *R*, which were determined both volumetrically and mass spectrometrically by the following experiments.

Volumetric Determination. Fifteen milliliters of solution containing approximately 2×10^{-4} mol of $(NC)_5FeNO^{2-}$ and N_3^- was photolyzed at wavelengths greater than 300 nm. The noncondensable fraction contained, after correction for a 3% impurity of O_2, 4.7×10^{-5} mol of nitrogen. The condensable fraction was 4.6×10^{-5} mol of nitrous oxide after correction for a 9% hydrazoic acid impurity. Both volume measurements assume ideal gas behavior. The ratio, R, was 1.02 ± 0.03.

Mass Spectrometric Determination. The entire gas output was collected as one sample and the relative proportions were calculated by using an intensive parameter, *B*, which may be defined as

$$B = \frac{\text{height of compound base peak}}{\text{height of } m/e \text{ 43 peak for } n\text{-butane}}$$

when the peak heights are normalized to the same introduction pressure. Values for *B* were determined from data taken on pure components under the same conditions on the mass spectrometer employed in analysis of the gaseous mixture. This is a necessary precaution since literature values[11] were found to vary significantly (*ca.* 10% and divergent) from those experimentally determined *ad hoc*. For nitrogen, the *B* at *m/e* 28 was 0.72 ($B^{28}_{N_2} = 0.72$) and for nitrous oxide at *m/e* 44 was 0.54 ($B^{44}_{N_2O} = 0.54$). Then

$$R = \frac{\text{peak height of } N_2}{B^{28}_{N_2}} \; \frac{B^{44}_{N_2O}}{\text{peak height of } N_2O}$$

with $R = 1.18$. Since the partial pressures of the individual gases were less than half the total pressures used in ascertaining the *B* values, the relative error is adjudged to be about 10% and the value of $R = N_2{:}N_2O$ is concluded to be 1 based on these experiments.

In order to determine the source of the oxygen in the N_2O, the following isotopic labeling experiments were carried out.

$(NC)_5FeNO^{2-} + N_3^-$ in $H_2{}^{18}O$. Sodium nitroprusside (0.0303 g, *ca.* 10^{-4} mol) and sodium azide (0.0068 g, *ca.* 10^{-4} mol) were dissolved in 20 ml of ^{18}O-enriched water (1.6 atom % ^{18}O). The nitrous oxide was collected and analyzed by mass spectrometer. The relative abundance of the *m/e* 46 peak was 0.25 (±0.03)% *vs.* the natural abundance of 0.204%.

$(NC)_5FeN^{18}O_2 + N_3^-$ in H_2O. Sodium azide (0.0138 g, 2.10×10^{-4} mol) was dissolved in 3 ml of water and added to the ^{18}O-enriched nitroprusside (2.1×10^{-4} mol in *ca.* 10 ml of H_2O, 0.93 ± 0.03 atom % ^{18}O) solution prepared as described previously. The resulting N_2O gave, upon mass spectral analysis, a relative abundance for the *m/e* 46 peak of 0.90 ± 0.05%, compared to 0.204% for nitrous oxide of normal isotopic composition. Thus it is clear that the oxygen of the N_2O comes from the oxygen of the NO moiety of $(NC)_5FeNO^{2-}$ and not from the water. The source of the nitrogen in N_2O and N_2 was determined from the following experiment.

$(NC)_5FeNO^{2-} + {}^{15}NNN^-$ in H_2O. One milliliter of a sodium azide solution (7.7% ^{15}N, 0.0435 g/ml), which was prepared from 0.4005 g of NaN_3 and 0.0346 g of 96.9% $Na{}^{15}NN_2$ dissolved in 10 ml of water, was added to 19 ml of a sodium nitroprusside solution (0.165 g of $Na_2[(NC)_5FeNO]\cdot 2H_2O$). The resulting gases were collected and purified by successive fractionation through Dry Ice–acetone and liquid N_2 traps. The corrected N_2O mass spectrum showed $[(m/e\ 45)/(m/e\ 44)] \times 100 = 3.6 \pm 0.2$ and $[(m/e\ 31)/(m/e\ 30)] \times 100 = 0.24 \pm 0.11$. The former ratio shows that half of the ^{15}N present in the N_3^- is incorporated in the N_2O; the N_3^- can attack nitroprusside with either a ^{15}N or ^{14}N terminal nitrogen. The latter ratio represents the $^{15}N^{16}O{:}^{14}N^{16}O$ ratio (normal-abundance ratio 0.36). This ratio, coupled with $(m/e\ 29)/(m/e\ 28)$ equals 3.0 ± 0.4, indicates that the primary source of the terminal nitrogen in N_2O is from the terminal nitrogen of the azide ion.

The iron-containing product is found to be $(NC)_5Fe^{II}H_2O^{3-}$ (see Kinetics section) and therefore the stoichiometry and isotopic distribution of oxygen for the initial reaction is given in eq 1.

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[5] D. X. West, *J. Inorg. Nucl. Chem.*, **30**, 1263 (1968).

[6] G. K. Rollefson and C. F. Oldershaw, *J. Amer. Chem. Soc.*, **54**, 977 (1932).

[7] D. F. Heath, *J. Chem. Soc.*, 4152 (1957).

[8] J. Milbauer and O. Vogel, *Chem. Listy*, **20**, 390 (1926).

[9] D. J. Kenney, T. P. Flynn and J. B. Gallins, *J. Inorg. Nucl. Chem.*, **20**, 75 (1961).

[10] S. K. Wolfe and J. H. Swinehart, unpublished data.

[11] A. Cornu and R. Massot, "Compilation of Mass Spectral Data," Heyden and Son, London, 1966.

Table I. Kinetic Study of the $(NC)_5FeNO^{2-}$–N_3^- Reaction[a]

Expt	$[(NC)_5FeNO^{2-}]$, M	$[N_3^-]$, M	Reaction 1a		Reaction 1b	
			$t_{1/2}$, sec	k_{1a}, M^{-1} sec^{-1}	$t_{1/2}$, sec	k_{1b}, sec^{-1}
a	0.050	0.50	6.3 ± 0.8	0.22 ± 0.04[b]	3.6 ± 0.6	0.19 ± 0.4[b]
b	0.025	0.50	6.0	0.23		
c	0.050	0.25	11.5	0.24	3.8 ± 0.3	0.18 ± 0.2[c]
d	0.005	0.025	100	0.28		
				Av 0.2		Av 0.2

[a] $T = 23°$, $\mu = 1.0$ (NaCl), pH 6.0 (phosphate), λ 510 nm. [b] Average of seven runs. [c] Average of two runs.

$$(NC)_5FeN^*O^{2-} + {}^{\ddagger}NNN^- + H_2O = (NC)_5Fe^{II}H_2O^{3-} + N_2 + {}^{\ddagger}NN^*O \qquad (1)$$

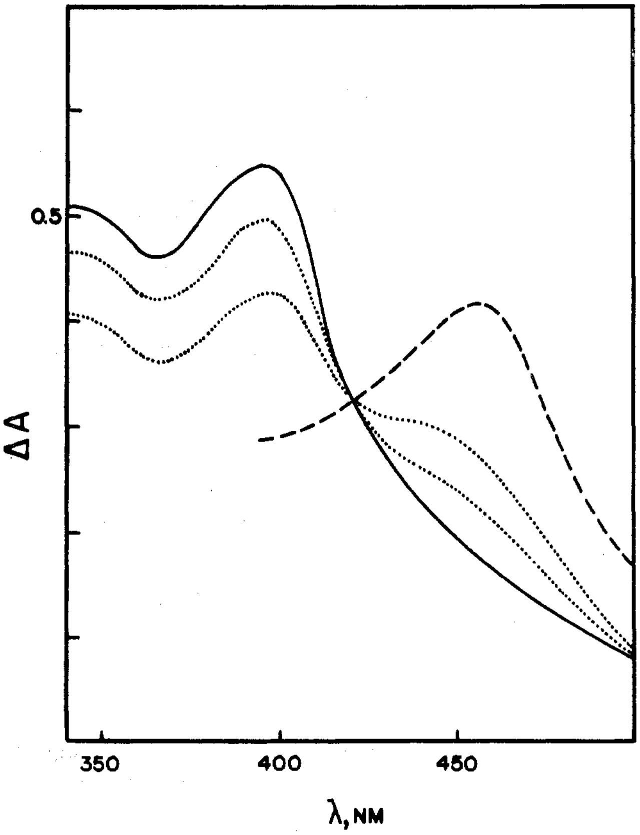

Figure 1. Monomer–dimer equilibration in the $(NC)_5Fe^{II}H_2O^{3-}$ system: · · · ·, spectrum during course of reaction; - - - -, resolved shoulder extrapolated to zero time; ——, final spectrum, representing dimer $(NC)_{10}Fe_2^{6-}$. $[(NC)_5FeNH_3^{3-}] = 8.3 \times 10^{-4}$ F (see text); deoxygenated solutions, $\mu = 1.0$ (NaCl), pH 6.0 (phosphate). Some contributions to the spectrum from oxidation products are present at small wavelengths.

Kinetics. When deoxygenated solutions containing $(NC)_5FeNO^{2-}$ and N_3^- are mixed, two consecutive reactions are observed. When the system was monitored at 510 nm, the first reaction (1a) exhibited a small absorbance decrease and the second reaction (1b) exhibited a large absorbance increase. The study was hindered by the time scales of the reactions and the absorbance changes involved. Both reactions 1a and 1b were *assumed* to be pseudo first order under the experimental conditions. The rate constant k_{1a} was estimated under conditions where (1a) was very slow compared to (1b) (expt d, Table I). Under these conditions (1a) becomes rate limiting and the intermediate formed in (1a) and consumed in (1b) (I) never attains a large concentration. Approximate values of k_{1b} were obtained by using the first-order plots of the final stages of (1b) under reaction conditions such that (1a) was of the order of (1b). This method is inaccurate and such rate constants should be considered as only order of magnitude numbers. The rate constant k_{1a} was calculated from the initial slopes after subtraction of (1b). It was found that k_{1a} calculated by such a process was in fair agreement with values calculated under conditions when (1a) was rate determining. The data are summarized in Table I. The rate law for reaction 1a is first order in $[(NC)_5FeNO^{2-}]$ and $[N_3^-]$, *i.e.*

$$d[I]/dt = k_{1a}[(NC)_5FeNO^{2-}][N_3^-]$$

where I is an iron-containing intermediate in reaction 1 and $k_{1a} = 0.2\ M^{-1}\ sec^{-1}$ at 23°. The rate law for the second reaction (1b) is independent of $[N_3^-]$ and is of the form

$$-d[I]/dt = k_{1b}[I]$$

with $k_{1b} = 0.2\ sec^{-1}$ at 23°.

The initial product of reaction 1b is $(NC)_5Fe^{II}H_2O^{3-}$, which is known to dimerize to give decacyanodiferrate(II), $(NC)_{10}Fe^{II}{}_2{}^{6-}$,[12] or to yield pentacyanoazidoferrate(II), $(NC)_5Fe^{II}N_3^{4-}$, if sufficient N_3^- is present to complex with the initial product. If oxygen is present, $(NC)_5Fe^{II}N_3^{4-}$ is oxidized to the well-established complex $(NC)_5Fe^{III}N_3^{3-}$, λ_{max} 560 nm.[13]

The presence of $(NC)_5Fe^{II}H_2O^{3-}$ as the iron-containing product after reaction 1b was established by comparison with the spectral properties[12] and chemistry of $(NC)_{10}Fe^{II}{}_2{}^{6-}$ which formed subsequent to the rapid aquation[14] of $(NC)_5Fe^{II}NH_3^{3-}$. When $Na_3[(NC)_5Fe^{II}NH_3]\cdot 3H_2O$ is dissolved in a pH 6 buffer solution (phosphate, $\mu = 1.0$ (NaCl)), a species with λ_{max} at 455 nm is initially observed (Figure 1). It rapidly disappears forming an isosbestic point at 420 nm with a new species that has λ_{max} at 395 nm and ϵ of *ca.* 940 M^{-1} cm^{-1} based on the initial concentration of $(NC)_5Fe^{II}NH_3^{3-}$. The second species is identifiable as the decacyanodiferrate(II) reported by Emschwiller and Jorgensen.[12] In a separate paper, Emschwiller[15] noted the appearance of a shoulder at *ca.* 440 nm upon the photolysis of $Fe(CN)_6^{4-}$ which he attributed to formation of pentacyanoaquoferrate(II), $(NC)_5Fe^{II}H_2O^{3-}$. Resolution of the shoulder in this work and extrapolation of absorbance to zero time with respect to solution preparation allowed assignment of λ_{max} for the iron(II)-aquo complex as 455 nm with an estimated molar absorptivity of 460 (±200) M^{-1} cm^{-1}.

Quantitative studies were performed which showed that addition of deoxygenated azide solutions to oxygen-free solutions of the iron(II) dimer, generated *via* the ammine, results in formation of a species which had λ_{max} at 440 nm (ϵ *ca.* 1400 M^{-1} cm^{-1}) (Figure 2A) and which formed isosbestic points with the original dimer spectrum at 380 and 405 nm, in agreement with a direct dimer–azide complex reaction.

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(13) B. Jaselskis, *J. Amer. Chem. Soc.*, **83**, 1082 (1961).
(14) J. M. Malin, personal communication.
(15) G. Emschwiller, *C. R. Acad. Sci., Ser. C*, **268**, 692 (1969).

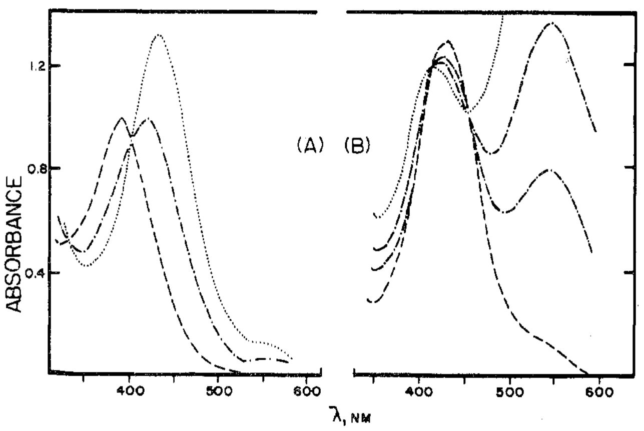


Figure 2. (A) Spectra in $(NC)_{10}Fe_2^{6-}$-N_3^- reaction: - - - - -, dimer spectrum; - · - · -, spectrum during course of reaction; · · · · ·, spectrum of final product, $(NC)_5FeN_3^{4-}$; in deoxygenated solution. (B) Spectra in $(NC)_5FeN_3^{4-}$-O_2 reaction: - - - - -, spectrum before oxidation; - · - · -, spectrum during course of reaction; · · · · ·, portion of spectrum of final product, $(NC)_5FeN_3^{3-}$; $\mu = 1.0$ (NaCl), pH 6.0 (phosphate).

The kinetic data of Table II indicate a rate law for $(NC)_5Fe^{II}N_3^{4-}$ formation, *i.e.*

$$d[(NC)_5Fe^{II}N_3^{4-}]/dt = k_2[(NC)_{10}Fe^{II}{}_2{}^{6-}][N_3^-]$$

with $k_2 = 1.0\ (\pm 0.1) \times 10^2\ M^{-1}\ sec^{-1}$ (23°). This information supports a simple two-step mechanism for conversion of the iron(II) dimer to the iron(II) azide complex

$$[(NC)_{10}Fe^{II}{}_2]^{6-} + N_3^- \xrightarrow{k_2} (NC)_5Fe^{II}N_3^{4-} + (NC)_5Fe^{II\,3-} \tag{2}$$

$$(NC)_5Fe^{II\,3-} + N_3^- \xrightarrow{\text{fast}} (NC)_5Fe^{II}N_3^{4-}$$

Subsequent to the formation of $(NC)_5Fe^{II}N_3^{4-}$, addition of oxygen results in appearance of the well-defined complex, $(NC)_5Fe^{III}N_3^{3-}$ (λ_{max} 560 nm), with isosbestic points at 420 and 460 nm (Figure 2B). The data in Table III indicate the rate law for formation of $(NC)_5Fe^{III}N_3^{3-}$ as

$$d[(NC)_5Fe^{III}N_3^{3-}]/dt = k_3[(NC)_5Fe^{II}N_3^{4-}][O_2]$$

with $k_3 = 3.0\ (\pm 0.7) \times 10^2\ M^{-1}\ sec^{-1}$ (23°). The reaction is

$$(NC)_5Fe^{II}N_3^{4-} + O_2 \xrightarrow{k_3} (NC)_5Fe^{III}N_3^{3-} + O_2^-, \text{etc.} \tag{3}$$

Qualitative oxidation experiments on $(NC)_5Fe^{II}N_3^{4-}$ show it to be easily oxidized by basic peroxide but not by thallous hydroxide. In acidic media it was oxidized by cuprous iodide. These half-reactions and their standard potentials are

$H_2O + HO_2^- + e^- = 2OH^- + OH$ $E° = -0.24\ V$

$Tl(OH) + e^- = OH^- + Tl$ $E° = -0.34\ V$

$CuI + e^- = Cu + I^-$ $E° = -0.18\ V$

Thus the standard potential for the half-reaction

$$(NC)_5Fe^{III}N_3^{3-} + e^- = (NC)_5Fe^{II}N_3^{4-}$$

is estimated to be *ca.* −0.3 (±0.1) V.

Table II. Kinetic Study of the Decacyanodiferrate(II)-Azide Reaction[a]

$10^4[(NC)_{10}Fe_2{}^{II\,6-}]$,[b] M	$[N_3^-]$, M	k_2,[c] $M^{-1}\ sec^{-1}$
1.0	0.025	92
1.0	0.0025	102
1.0	0.00125	102
2.0	0.025	100

[a] $T = 23°$, $\mu = 1.0$, pH 6.0. [b] Based on formal concentration of $Na_3[(NC)_5FeNH_3]\cdot 3H_2O$; see text. [c] Relative error, ±10%. Average of three runs.

Table III. Kinetic Study of the $(NC)_5Fe^{II}N_3^{4-}$-O_2 Reaction[a]

$10^5[(NC)_5Fe^{II}N_3^{4-}]$, M	$10^4[O_2]$, M	$10^{-2}k_3$, $M^{-1}\ sec^{-1}$	
5.0	5.0 (±0.4)	2.8 (±0.2)[b]	(3)[c]
5.0	2.5 (±0.3)	3.2 (±0.4)	(3)
5.0	0.8 (±0.2)	4.3 (±1)	(1)
5.0	1.6 (±0.4)	4.0 (±1)	(1)
5.0	9 (±2)	2.6 (±0.5)	(3)
10	5.0 (±0.2)	2.5 (±0.2)	(3)

[a] $T = 23°$, $\mu = 1.0$ (NaCl); followed at λ 560 nm. [b] Estimated error limits. [c] Number of runs.

Nitroprusside-Hydroxylamine Reaction. Stoichiometry and Isotopic Experiments. The reaction between $(NC)_5FeNO^{2-}$ and NH_2OH in basic solutions produces N_2O. The following experiments were carried out to determine the stoichiometry of the reaction. (a) Fifteen milliliters of 1 *M* NaOH, 1.5×10^{-2} mol of NaOH, was added to 2.0×10^{-3} mol of sodium nitroprusside and 2.6×10^{-4} mol of hydroxylamine hydrochloride. The gas was trapped with a liquid nitrogen trap; then the volume was determined on the vacuum line: found, 2.1 (±0.2) × 10^{-4} mol of nitrous oxide. No other gases were observed as determined by mass spectral analysis. (b) Fifteen milliliters of 1 *M* NaOH was added to 2.0×10^{-4} mol of sodium nitroprusside and 2.0×10^{-3} mol of hydroxylamine hydrochloride. In this case NH_3 was also produced *via* the disproportionation of excess NH_2OH

$$4NH_2OH = 2NH_3 + N_2O + 3H_2O$$

Total N_2O produced was 3.8×10^{-4} mol, and after correction for disproportionation 2.1 (±0.2) × 10^{-4} mol of N_2O was found from the $(NC)_5FeNO^{2-}$-NH_2OH reaction.

The following isotopic labeling experiments were performed to determine the source of the nitrogen and oxygen in the N_2O.

$(NC)_5FeN^{18}O^{2-}$ + NH_2OH. A solution of isotopically enriched $(NC)_5FeN^{18}O^{2-}$ was divided into two parts: one part for reaction with azide to determine the state of enrichment of the nitroprusside and the other for reaction with unlabeled hydroxylamine hydrochloride. Reaction with azide gave a relative abundance of the *m/e* 46 peak due to nitrous oxide of 0.81 ± 0.05%. The nitroprusside then is also 0.81 ± 0.05% ^{18}O enriched. Reaction of the labeled nitroprusside with hydroxylamine hydrochloride and base gave nitrous oxide of relative abundance for *m/e* of 0.22 ± 0.03% (*vs.* the natural abundance of 0.204%).

$(NC)_5FeNO^{2-}$ + $NH_2{}^{18}OH$. To sodium nitroprusside (*ca.* 10^{-4} mol) and hydroxylamine hydrochloride (0.65 ± 0.05% ^{18}O enriched, *ca.* 10^{-4} mol) was added 10 ml of 0.1 *M* NaOH. The nitrous oxide which resulted had *m/e* 46 with relative abundance 0.56 ± 0.05.

HNO_2 + $NH_2{}^{18}OH\cdot HCl$. Normal sodium nitrite (natural abundance 0.204 atom % ^{18}O each oxygen, 0.07 g, 10^{-3} mol) was dissolved in 20 ml of H_2O at room temperature. The pH was adjusted to *ca.* 3.5 by dropwise addition of dilute HCl. Isotopically enriched hydroxylamine hydrochloride (0.65 ± 0.05% ^{18}O enriched, 0.07 g, 10^{-3} mol) dissolved in 10 ml of H_2O was added and the gaseous product collected on the vacuum line. The mass spectrum revealed only N_2O production, with a relative abundance at *m/e* 46 of 0.43 ± 0.04%. This is midway between the normal isotopic abundance

Table IV. Kinetics of the $(NC)_5FeNO^{2-}$-NH_2OH Reaction[a]

10^4-[$(NC)_5$-$FeNO^{2-}$], *M*	10^3-[NH_2-$OH\cdot$HCl], *M*	10^2-[OH^-],[b] *M*	*T*, °C	$10^{-5}k_{4a}$, M^{-2} sec^{-1}	
4.00	2.0	0.27	26	4.62 ± 0.20	(4)[c]
4.00	3.0	0.27	26	4.68 ± 0.14	(3)
4.00	4.0	0.27	26	4.45 ± 0.11	(4)
20.0	0.4	0.25	23	3.7	
40.0	0.4	0.24	23	3.6	
4.0	2.0	0.22	23	4.2	
4.0	2.0	1.4	23	3.9 ± 0.1	(2)
4.0	2.0	3.4	23	3.6 ± 0.3	(2)

[a] $\mu = 1.0$ (NaCl), λ 440 nm. [b] [OH^-] computed from pH and a value of 1.4×10^{-14} for the dissociation constant of water at $\mu = 1.0$. [c] Number of runs used in computing average and standard deviation in parentheses.

(0.204%) and that of the enriched species, indicative of a symmetric intermediate and that no preferential labeling had occurred.

$(NC)_5FeNO^{2-}$ + $^{15}NH_2OH{\cdot}HCl$. The reaction was conducted in the same manner as the previous experiment utilizing 5.2 (±0.2)% ^{15}N-enriched hydroxylamine prepared as described (*vide supra*). The ratio of the relative abundance of the *m/e* 31 to the *m/e* 30 peak was 0.051 (±0.003). The calculated ratio for $^{15}N^{14}NO$ is 0.005 (±0.001) and for $^{14}N^{15}NO$ is 0.053 (±0.005) and, therefore, the product is identified as $^{14}N^{15}NO$. The calculations are based on mass spectral investigations of nitrous oxide isotopes performed by Begun and Landau.[16]

The foregoing experiments show the stoichiometry and isotopic labeling with respect to nitrogen and oxygen to be

$$(NC)_5FeNO^{2-} + {}^{\ddagger}NH_2{}^{*}OH + OH^- = (NC)_5Fe^{II}H_2O^{3-} + N^{\ddagger}N^{*}O + H_2O \qquad (4)$$

with the oxygen and central nitrogen of N_2O coming from hydroxylamine.

Kinetics. A series of kinetic experiments on the $(NC)_5FeNO^{2-}$-NH_2OH reaction were performed on the stopped-flow apparatus by monitoring transmittance at 440 nm and the results are reported in Table IV. Plots of the observed rate constants *vs.* hydroxide ion concentration at constant hydroxylamine concentration and *vs.* hydroxylamine concentration at constant hydroxide concentration were linear. The concentration of free hydroxylamine was determined using an acid dissociation constant for NH_3OH^+ of 1.5×10^{-6}.[17] From the data in Table IV the rate law is formulated to be

$$d[J]/dt = k_{4a}[(NC)_5FeNO^{2-}][NH_2OH][OH^-] \qquad (4a)$$

where J is an intermediate in reaction 4. The Arrhenius activation energy, E_a, was determined to be 9.5 ± 1.0 kcal/mol from the following average rate constants, k_{4a}, at various temperatures: $(1.8 \pm 0.1) \times 10^5$ M^{-2} sec^{-1} (9.5°), $(3.8 \pm 0.2) \times 10^5$ (23.0°), $(4.6 \pm 0.2) \times 10^5$ (26.0°), $(7.3 \pm 0.9) \times 10^5$ (35.2°); k_{4a} is 4.5×10^5 M^{-2} sec^{-1} at 25°.

The species J decomposes rapidly to yield $(NC)_5Fe^{II}H_2O^{3-}$, which was identified as it was in the $(NC)_5FeNO^{2-}$-N_3^- reaction. The spectrum of species J was obtained by extrapolation of oscilloscope traces from the stopped-flow apparatus and is recorded in Figure 3 (λ_{max} 445 nm and ϵ_{445nm} >700 M^{-1} cm^{-1}). An attempt was made to generate $(NC)_5Fe^{II}N_2O^{3-}$, assuming this to be possibly species J, by applying N_2O at high pressures to solutions of $(NC)_{10}Fe^{II}{}_2{}^{6-}$. However no spectral change of the solution was observed.

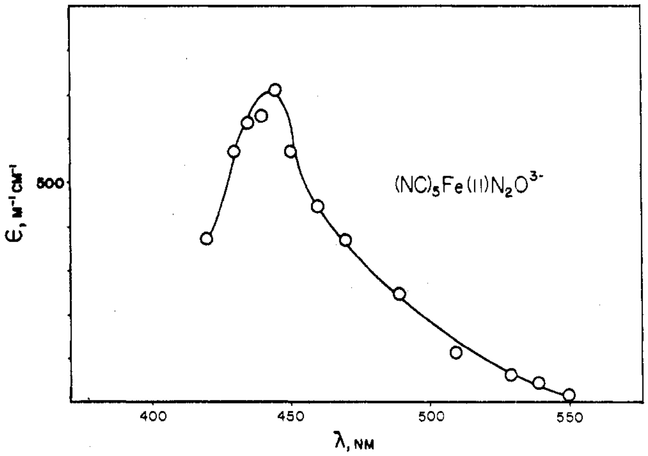
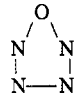


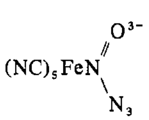
Figure 3. Spectrum of intermediate J in $(NC)_5FeNO^{2-}$-NH_2OH-OH^- reaction.

Discussion

Nitroprusside-Azide Reaction. Stoichiometric and isotopic experiments indicate that the net reaction is represented by eq 1. The oxygen of N_2O comes from the oxygen of the NO moiety of $(NC)_5FeNO^{2-}$ and the terminal nitrogen comes from the terminal nitrogen of the azide ion. The mode of decomposition of the intermediate formed in the $(NC)_5FeNO^{2-}$-N_3^- reaction is different from that observed for the *trans*-$RuCl(das)_2NO^{2+}$-N_3^- reaction.[18] In the latter case a cyclic intermediate



(either bound to or free of the Ru) is proposed, which breaks statistically at either N-O bond. In the $(NC)_5FeNO^{2-}$-N_3^- reaction either no such intermediate is formed or, if it is formed, N-O bond breakage is not at the bond adjacent to the Fe-N bond. The mechanism suggested by the rate laws (1a) and (1b) is the direct addition of N_3^- to nitroprusside to form



$$(NC)_5Fe\overset{O^{3-}}{\underset{N_3}{N}}$$

followed by the decomposition of this species to give $(NC)_5FeH_2O^{3-}$, N_2O, and N_2. The rate constant for the formation of the adduct, k_{1a}, of 0.2 M^{-1} sec^{-1} is comparable with that for the reaction of $(NC)_5FeNO^{2-}$ with OH^- (0.55 M^{-1} sec^{-1} at 25°)[4] but is considerably smaller than that for the $(NC)_5FeNO^{2-}$-HS^- reaction (170 M^{-1} sec^{-1} at 25°).[19] However the HS^- anion is more polarizable (attacking side of HS^- is larger) than either OH^- or N_3^- and the bond-making addition reaction would be expected to have a lower activation energy requirement in the HS^- case.

The value determined for the couple

$$(NC)_5FeN_3{}^{3-} + e^- = (NC)_5FeN_3{}^{4-}$$

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of −0.3 ± 0.1 V is a great deal more negative than those previously reported for other cyanoferrate(II)–cyanoferrate(III) couples

$$(NC)_5FeNO_2{}^{3-} + e^- = (NC)_5FeNO_2{}^{4-} \quad E = +0.52^{20,21}$$

$$Fe(CN)_6{}^{3-} + e^- = Fe(CN)_6{}^{4-} \quad E = +0.36^{21} \qquad (5)$$

Results obtained in this work indicate that the potential of +0.37 V reported for the couple

$$(NC)_5FeNH_3{}^{2-} + e^- = (NC)_5FeNH_3{}^{3-\ 20,21} \qquad (6)$$

was probably due to the couple

$$(NC)_{10}Fe^{II}{}_2{}^{5-} + e^- = (NC)_{10}(Fe^{II}Fe^{III})^{6-}$$

The mixed-iron dimer has been reported by Emschwiller and Jorgensen.[12] The similarity in potentials for eq 5 and 6 is also in agreement with this analysis and allows for greater consistency in that the more positive reduction potentials reflect the necessity for ligands which can accept electron density from the metal t_{2g} orbitals to stabilize the low-spin iron(II) species. The nephelauxetic effect of other ligands such as SCN^- and $N_3{}^-$ can enhance the rate of oxidation by providing greater steric availability of the t_{2g} orbitals.[22] In the case of metal-ligand complexes where the ligand has filled orbitals of symmetry characteristics similar to those of the metal t_{2g} orbitals, *e.g.*, M-N_3 and M-SCN, the repulsion between the metal d_{xz}, d_{yz} orbitals and the ligand $p\pi$ orbitals is reduced by oxidation from the d^6 to the d^5 state.

It is important to note that variation of the sixth ligand, X^n, in complexes of the type $(NC)_5Fe^{II}X^{-3+n}$ can drastically alter the standard potential, $\mathcal{E}°$, of the couple

$$(NC)_5Fe^{III}X^{-2+n} + e^- = (NC)_5Fe^{II}X^{-3+n}$$

These changes in $\mathcal{E}°$ can alter the reactivity of the iron(II) complex toward oxygen. For example $Fe(CN)_6{}^{4-}$ does not react with oxygen, but both $(NC)_5FeN_3{}^{4-}$ and $(NC)_5FeSCN^{4-}$ do. These facts may have important implications with respect to the oxygen oxidations of biologically important iron(II) complexes.

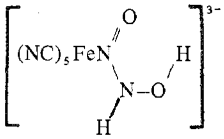
Nitroprusside-Hydroxylamine Reactions. Stoichiometric and isotopic labeling experiments show the net reaction to be represented by eq 4. The oxygen and central nitrogen of the N_2O came from the hydroxylamine. In part, the mechanism is elucidated by the rate law, eq 4a, which shows the rate of formation of the intermediate, J, in reaction 4 to be first order in $(NC)_5FeNO^{2-}$, NH_2OH, and OH^-. Such a rate law suggests a preequilibrium between two of the species, forming an intermediate, followed by a rate-determining attack of the third species on the intermediate.

The possibilities that the initial interaction is between $(NC)_5FeNO^{2-}$ and OH^- and between NH_2OH and OH^- can be eliminated. The kinetics of the $(NC)_5FeNO^{2-}$-OH^- reaction

$$(NC)_5FeNO^{2-} + 2OH^- = (NC)_5FeNO_2{}^{4-} + H_2O$$

have been examined.[4] The rate law is first order in $(NC)_5FeNO^{2-}$ and OH^- with a bimolecular rate constant of 0.6 M^{-1} sec^{-1} at 26° or a half-life for the reaction at $[OH^-] = 2.7 \times 10^{-3}$ M of 430 sec, which compares with the half-life of the $(NC)_5FeNO^{2-}$-NH_2OH-OH^- reaction of a few tenths of 1 sec. Since there is persuasive evidence (activation parameters and comparative rate constants for other $(NC)_5FeNO^{2-}$-B^n reactions[1,4]) that the bimolecular rate constant for the $(NC)_5FeNO^{2-}$-OH^- reaction is that for the addition of OH^- to the NO moiety of $(NC)_5FeNO^{2-}$, the $(NC)_5FeNO^{2-}$-OH^- reaction cannot therefore be forming an intermediate which is reactive toward NH_2OH. The possibility of NH_2OH-OH^- interaction prior to reaction with nitroprusside can be considered remote on the basis of the low acidity of the hydroxylamine moiety and the specific labeling observed in the isotopic experiments.

It is well established that bases add to nitroprusside; thus it seems likely that NH_2OH adds to the NO moiety of $(NC)_5FeNO^{2-}$ to form an adduct which is then attacked by OH^-. Loss of a proton would result in the formation of



The kinetics do not define species J, but further proton shifts (intramolecular and to the solvent) could result in formation of hyponitrite anions, $HN_2O_2{}^-$ or $N_2O_2{}^{2-}$, bound to the metal center. If these latter species are present, coordination to the pentacyanoferrate(II) center must activate the coordinated nitrogen of the hyponitrite moiety to decomposition *via* oxygen loss preferential to isomerization of the nitrogen coordination site, since we have shown that the nitrous oxide produced always contains oxygen derived only from the hydroxylamine reactant. This specificity of labeling gives some evidence for the existence of a nitrous oxide adduct. The spectrum of the intermediate J (Figure 3) has λ_{max} at 445 nm. This compares well with that observed here for the isoelectronic pentacyanoazidoferrate(4−) complex, which has λ_{max} at 440 nm. An N_2O adduct $[RuCl(das)_2N_2O]^+$ was isolated from the *trans*-$RuCl(das)_2NO^{2+}$-NH_2OH reaction.[18]

Although the detailed kinetics of the decomposition of species J to $(NC)_5Fe^{II}H_2O^{3-}$ and N_2O were not examined, the half-life for this decomposition was on the order of several seconds at 35.2°. This is approximately 1000 times faster than the decomposition of hyponitrite at the same pH. The enhancement may be larger if the decomposition of nitrous oxide complex is being observed.

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Registry No. $(NC)_5FeNO^{2-}$, 15078-28-1; $N_3{}^-$, 14343-69-2; $(NC)_{10}Fe_2{}^{6-}$, 28850-28-4; $(NC)_5FeN_3{}^{4-}$, 22337-20-8; $(NC)_5FeN_3{}^{3-}$, 19512-93-7; NH_2OH, 7803-49-8; $(NC)_5FeH_2O^{3-}$, 18497-51-3.

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