

The Reaction of Nitrogen Dioxide with Iron(III) Cyanide Complexes

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The kinetics of reaction of $[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$ with nitric and nitrous acids has been shown to fit the following rate law:

$$\text{rate} = k h^{1/2} [\text{HNO}_2]^{1/2} [\text{nitrate}]^{1/2} [\text{Fe}_2^{\text{III}}(\text{CN})_{10}^{4-}]$$

The primary product appears to be a binuclear Fe^{III} , Fe^{II} cyanide complex, with an NO^+ ligand in the coordination shell of the ferrous iron. The kinetics of reaction and the properties of the product show a close resemblance to those of the reaction of $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ with nitric and nitrous acids under similar conditions. The kinetics of reaction of $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{phen})]^-$ and $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]^-$ with nitric and nitrous acids follow a similar rate law, though the dependence of rate upon acidity and nitrate concentration has not been determined.

$$\text{Rate} = k [\text{HNO}_2]^{1/2} [\text{complex}]$$

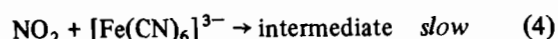
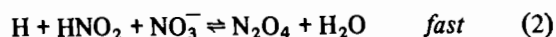
It is concluded that the reaction of iron(III) cyanide complexes with nitric and nitrous acids to form iron(II) cyano nitrosyl products occurs through NO_2^+ as the active nitrogen species.

Introduction

We have previously [1] examined the mechanism of the reaction between the ferricyanide ion and nitric and nitrous acids, under conditions similar to those used in a preparative procedure for sodium nitroprusside [2]. Reaction was shown to proceed through the formation of an intermediate, which slowly decomposed. The intermediate species was stable enough to be isolated as the silver salt, and was identified as a dimeric iron(II) cyanonitrosyl complex $[(\text{CN})_5\text{Fe}^{\text{II}}\mu(\text{NO})\text{Fe}^{\text{II}}(\text{CN})_4\text{NO}]^{3-}$, with the terminal nitrosyl group *cis* to the bridging nitrosyl species. The rate law took form (1): $2[\text{Fe}(\text{CN})_6]^{3-} + \text{HNO}_3 + \text{HNO}_2 + \text{H}_2\text{O} + 5\text{H}^+ \rightarrow [(\text{CN})_5\text{Fe}^{\text{II}}\mu(\text{NO})\text{Fe}^{\text{II}}(\text{CN})_4\text{NO}]^{3-} + 2\text{NH}_4^+ + 2\text{CO}_2 + \text{HCN}$

$$\text{rate} = k h^{1/2} [\text{HNO}_2]^{1/2} [\text{nitrate}]^{1/2} [\text{Fe}(\text{CN})_6^{3-}] \quad (1)$$

This rate law was interpreted as a rate determining attack by nitrogen dioxide upon ferricyanide, (4).



In this reaction the nitrogen dioxide performs three functions:

(i) it reduces Fe^{III} to Fe^{II} ; (ii) it oxidises CN^- to OCN^- , (which in acidic solution yields ammonia and carbon dioxide) (iii) it provides the NO^+ groups for the product. This appears to be a very unusual reaction, and we have extended our studies to see if a similar process can be observed for other iron(III) cyanide complexes.

Experimental

Materials

The dimer $[\text{Fe}_2^{\text{II}}(\text{CN})_{10}]^{4-}$ was prepared by the method of Emschwiller [3], and purified by passage through a column of Sephadex G25. The visible spectrum was in close agreement with literature data [4], and this was used as a criterion of purity. The complexes $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4(\text{phen})]$ and $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]$ were prepared and purified by the method of Schilt [5]. Aqueous solutions were stored in the refrigerator when not in use.

Kinetic Methods

The reaction was in all cases studied spectrophotometrically, using a cell in a thermostatted cell compartment of a Unicam SP500. The wavelengths used were 570 nm ($[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$), 500 nm ($[\text{Fe}^{\text{III}}(\text{CN})_4(\text{phen})]^-$) and 415 nm ($[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]^-$). In order to check for possible decomposition in acidic solution by hydrolytic or other reactions, we measured the spectrum of solutions of various complexes in 5 M nitric acid + sulphamic acid (to destroy any traces of nitrous acid). There was

TABLE I. Kinetic Data on the Reaction of $[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$ with 5 M Nitric Acid at 25 °C.

$[\text{HNO}_2] = 0.1 \text{ M}$ $10^5 [\text{Fe}_2^{\text{III}}(\text{CN})_{10}^{4-}] / \text{M}$	$10^4 k_1 / \text{s}^{-1}$	$10^5 [\text{Fe}_2^{\text{III}}(\text{CN})_{10}^{4-}] = 10.8 \text{ M}$ $10^2 [\text{HNO}_2] / \text{M}$	$10^4 k_1 / \text{s}^{-1}$
1.73	4.22	1.5	1.92
4.33	4.33	5.0	3.12
8.66	4.33	10.0	4.67
13.0	4.45	15.0	5.47
17.3	4.63		

negligible change over the period of time used in the kinetic studies.

Mössbauer Spectra

Dried samples of the precipitated silver salt were submitted to the PCMU, Harwell for Mössbauer spectra and computer analysis of the results.

X-Ray powder photographs

These were obtained from a Guinier de Wolff No. II camera.

Mass Spectra

These were run on an MS-9 instrument.

Results

Most experiments were carried out in 5 M nitric acid at 25 °C.

$[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$, Kinetics

For this compound reaction could be followed by the fading of the characteristic blue colour of the complex and the kinetics were followed at 570 nm using solutions with a large excess of nitrous acid. The absorbance A decreased to zero, and plots of $\ln A$ vs. time were linear and yielded a pseudo first order rate constant k_1 , which was constant over a tenfold variation in $[\text{Fe}_2^{\text{III}}(\text{CN})_{10}^{4-}]_0$, thus confirming the first order behaviour. Variation of the nitrous acid concentration by a factor of ten yielded a plot of $\log k_1$ vs. $\log [\text{HNO}_2]$ with a slope of 0.49, showing that, as in the case of ferricyanide, reaction is half order with respect to nitrous acid. Data is shown in Table I. The dependence of rate upon acidity and upon nitrate concentration is more difficult to establish, because nitric acid is only a moderately strong acid, and in the concentration range of interest is only partly dissociated (81% in 5 M solution). Thus addition of perchloric acid or of sodium nitrate will cause a change in the degree of ionisation. Experiments carried out over the range 3 to 5 M perchloric acid with 1.0 M sodium nitrate and 0.1 M sodium nitride added gave a plot of $\log k_1$ vs. $(-H_0)$ of slope

0.41. A plot against $(-H_0)$ gave a slope of 0.54. We conclude that the reaction is half order with respect to protonating power, as measured by these acidity functions [6]. Experiments in 5 M perchloric acid + 0.1 M sodium nitrite and with 0.5, 0.75 and 1.0 M added sodium nitrate gave a plot of $\log k_1$ vs. $\log [\text{nitrate}]$ with a slope of 0.50. The results thus yield a rate law very similar to that observed for ferricyanide, eqn. (1).

$$\text{rate} = k h_2^{1/2} [\text{HNO}_2]^{1/2} [\text{nitrate}]^{1/2} [\text{Fe}_2^{\text{III}}(\text{CN})_{10}^{4-}] \quad (5)$$

At 25 °C for 5 M perchloric acid, $10^5 \times k = 5.95 \text{ mol l s}^{-1}$. Because of the problem of deciding which acidity function to use, and allowing for partial ionisation of nitric acid it seems desirable to quote the rate for our standard conditions, 5 M nitric acid at 25 °C in eqn. (6)

$$\text{rate} = 0.00139 [\text{HNO}_2]^{1/2} [\text{Fe}_2^{\text{III}}(\text{CN})_{10}^{4-}] \text{ mol l}^{-1} \text{ s}^{-1} \quad (6)$$

Measurements over the temperature range 7.8 to 34.2 °C for reaction in 5 M nitric acid gave a good Arrhenius plot, yielding an activation energy of $66 \pm 1 \text{ kJ mol}^{-1}$.

$[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$, Products

The infinity solution was a pale yellow colour, and no new peaks could be detected in the visible spectrum. The intense absorption of 5 M nitric acid in the near u.v. prevented measurements in that region. The reaction product(s) could be isolated by the addition of silver nitrate which produced a flocculent green/brown precipitate. Samples were precipitated from aliquots taken from a large batch of reaction mixture at times of 2.5 and 24 hours. The infra red spectrum of the silver precipitate showed an intense peak at 1950 cm^{-1} similar to that observed for $\text{Ag}_2\text{-Fe}^{\text{II}}(\text{CN})_5\text{NO}$ and $\text{Ag}_3\text{Fe}_2^{\text{II}}(\text{CN})_9(\text{NO})_2$ and sharp cyanide peaks at 2150 and 2070 cm^{-1} . X-Ray powder diffraction measurements gave very poor photographs, and attempts to obtain more crystalline samples by varying the conditions of precipitation were not successful. Mass spectrometric analysis of the gases evolved from the reaction mixture showed

peaks at $m/e = 44$ and 52 , thought to be due to CO_2 and C_2N_2 respectively. The most valuable evidence comes from an analysis of the Mössbauer spectrum of the precipitated silver salts, and these results are shown in Table II. An authentic sample of $\text{Ag}_2\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}$ gave a centre shift (relative to Fe) of $\delta = -0.19 \text{ mm s}^{-1}$ and a quadrupole splitting Δ of 1.84 mm s^{-1} . A sample of $\text{K}_4\text{Fe}_2^{\text{III}}(\text{CN})_{10}$ had $\delta = -0.135$ and $\Delta = 2.05 \text{ mm s}^{-1}$.

$[\text{Fe}^{\text{III}}(\text{CN})_4(\text{phen})]^-$ and $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]^-$
Kinetics

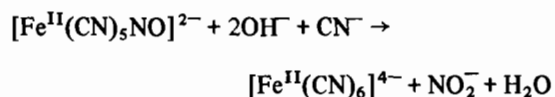
These complexes reacted very slowly with nitric and nitrous acids, even with relatively high concentrations of nitrous acid (up to 0.4 M). At these concentrations nitrous acid is not very stable, and so it was not possible to follow reaction beyond the early stages. Our studies were therefore restricted to measurements of the initial rate of change of absorbance at selected wavelengths. Pseudo first order rate constants obtained from plots of $\log A$ vs. time were independent of the concentration of complex over a four-fold variation in initial concentration, and plots of $\log k_1$ against $\log [\text{HNO}_2]$ gave slopes of 0.58 and 0.55 for the phenanthroline and bipyridyl complexes respectively. Attempts to determine the variation in rate with acidity, and with nitrate concentration proved unsuccessful. We could not vary the concentrations over a wide enough range to obtain satisfactory orders of reaction. Thus the results fit the eqn. (7)

$$\text{rate} = k_1 [\text{complex}] = k_2 [\text{HNO}_2]^{1/2} [\text{complex}] \quad (7)$$

with $10^4 k_2/\text{mol l}^{-1} \text{ s}^{-1} = 1.04$ (bipy) and 0.85 (phen) for 5 M nitric acid at 25°C . We presume that k_2 is also a function of acidity and of nitrate concentration.

$[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]^-$, Products

Attempts to isolate the products by precipitation techniques and by solvent extraction were unsuccessful. We also attempted to obtain spectrophotometric evidence by treating an 'infinity' solution with sodium carbonate to neutralise most of the nitric acid, and then adding excess sodium hydroxide + sodium cyanide. It is known that iron(II) cyano nitrosyl complexes react with alkali and cyanide ion to form the iron(II) cyano complex + nitrite ion:



Thus if our product was $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}(\text{bipy})]$ this reaction might give rise to $[\text{Fe}(\text{CN})_4(\text{bipy})]^{2-}$, a species of known spectrum. The reaction solution

TABLE II. Mössbauer Parameters (77 K) for Silver Salts Precipitated at Various Times t_p .

t_p hr	Species	δ mm s^{-1}	Δ mm s^{-1}	Abundance %
2	a_1	-0.19	1.77	42
	b_1	-0.05	1.71	14
	c_1	+0.49	0.75	44
5	a_2	-0.14	1.84	30
	b_2	-0.08	1.64	40
	c_2	+0.54	0.47	27
24	d_2	+0.39	1.84	3
	a_3	-0.34	2.14	14
	b_3	-0.11	1.67	53
	c_3	-0.05	1.19	20
	d_3	+0.38	1.73	13

obtained from $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]^-$ when treated in this way give a spectrum with a peak at 480 nm , compared with a peak for authentic $[\text{Fe}(\text{CN})_4(\text{bipy})]^{2-}$ at 482 nm .

$[\text{Fe}^{\text{III}}(\text{CN})_2(\text{phen})_2]^+$ and $[\text{Fe}^{\text{III}}(\text{CN})_2(\text{bipy})]^+$

The procedure recommended by Schilt for preparing these complexes involves boiling the corresponding iron(II) compounds with concentrated nitric acid. We take this as evidence that any reaction with NO_2 of the type we are studying must be very slow.

Discussion

The kinetic results for the reaction of $[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$ with nitric acid and nitrous acid parallel exactly those reported earlier for the reaction of $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ in a similar medium. The half order dependence of rate upon acidity, on the concentration of nitrous acid and of nitrate seems to point uniquely to a mechanism involving nitrogen dioxide as a reagent, as was discussed in a previous paper. The evidence for $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{phen})]^-$ and $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]^-$ is less complete, but the dependence of rate upon $[\text{HNO}_2]^{1/2}$ is again consistent with a mechanism involving nitrogen dioxide.

The most significant information about the structure of the product obtained from $[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$ comes from the Mössbauer spectrum of the silver salt precipitated from the infinity solution. It is clear that a number of different types of environment for the iron nucleus are present, computer analysis suggesting at least four species. When several species are present with overlapping spectra, there is some uncertainty in the values of the Mössbauer parameters and the estimate of relative amounts of the various

species because of the limitations in curve fitting procedures. The samples taken at 2 hours, 5 hours and 24 hours were all taken from the same batch of reaction mixture, and isolated in the same way. The earliest sample, (2 hour) appears to contain two species in essentially equal amounts, a_1 and c_1 (42% and 44%) and a smaller amount of third species b_1 (14%) (see Table II). In the 5 hour sample there are again two species a_2 and c_2 in essentially equal amounts of 30% and 27%). Sample a_2 has similar parameters to a_1 and is surely identical. The fact that b_2 and b_1 have similar parameters suggests that they are identical too. It would seem most probable that c_2 is the same as c_1 , though there is a marked difference in the value of Δ , though not of δ . We think this is due to the limitations of curve fitting procedures in our type of system. Looking now at the 24 hour sample we see that b_3 appears to be similar to b_2 and b_1 , and is presumably the same species, and that d_3 is very similar to the species d_2 which appeared as a very minor component in the 5 hour sample. It would be reasonable to expect a_3 and c_3 to be similar to a_2 and c_2 , but the Δ and δ values do not agree at all. It may be that after standing for 24 hours the species a_2 and c_2 have been completely destroyed and new products have appeared. If a fifth component had been formed, then presumably fitting the spectrum to a four component set of equations would presumably produce errors in the parameters deduced for the minor constituents. We do not wish to speculate further on this point. If we write $a \equiv a_1, a_2, b \equiv b_1, b_2, b_3, c \equiv c_1, c_2$, and $d \equiv d_2, d_3$, then we suggest that the initial products of reaction are a and c formed in equal amounts, and that on standing a and c decompose in equal amounts to form b . We think d is a product formed later in the reaction possibly from b .

Turning now to the chemical nature of a and c we note that the Mössbauer parameters of a are very similar to those of authentic silver nitroprusside, and we suggest a is an iron(II) cyanonitrosyl species. This conclusion is strengthened by the infra-red spectrum of the silver precipitate, which shows an intense nitrosyl stretching bond at 1950 cm^{-1} , very similar to that in $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]^{2-}$ and $[(\text{CN})_5\text{Fe}^{\text{II}}\mu(\text{NO})\text{Fe}^{\text{II}}(\text{CN})_4\text{NO}]^{3-}$. The identity of c is much less certain. It seems likely that the occurrence of a and c in equal amounts derives from the two iron atoms in $[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$. The evidence cited above suggests that a is an iron(III) species. The centre shift values (δ) for iron(III) low spin complexes are remarkably insensitive to variations in ligand properties within a series of similar compounds, and the quadrupole splittings (Δ) have not been readily rationalised [7]. It is thus difficult to use the spectra to make deductions about the structure. Mössbauer parameters for iron salts vary with

temperature, and with the nature of the counterion. The values for $[\text{Cs}_3\text{Fe}^{\text{III}}(\text{CN})_6]$ and $[\text{Ag}_3\text{Fe}^{\text{III}}(\text{CN})_6]$ are 0.470 (80 K) and 0.858 (147 K) seem comparable with those observed for c , though the δ values of -0.037 and -0.094 do not agree. We think that c is an iron(III) cyano species.

We must also consider whether a and c are part of a binuclear product derived from $[\text{Fe}_2^{\text{III}}(\text{CN})_{10}]^{4-}$ or whether they are separate species and the attack of NO_2 has resulted in breaking both of the cyanide bridges. If product b is derived from the initial product of reaction $a + c$, then the fact that a and c disappear in equivalent amounts suggests that they are part of a binuclear complex. Our previous work on $[(\text{CN})_5\text{Fe}^{\text{II}}\mu(\text{NO})\text{Fe}^{\text{II}}(\text{CN})_4(\text{NO})]^{3-}$ showed that a bridging NO^+ ligand produced a nitroprusside-like environment on both irons, so as c is definitely not nitroprusside like we assume that the bridging ligand in our binuclear product is probably cyanide ion. The Mössbauer parameters for b are definitely like those of nitroprusside, so we suggest that the decomposition of $a + c$ involves the conversion of the ferricyanide-like c half of the initial product to nitroprusside like product again possibly by attack of NO_2 . To illustrate what we mean, our first product c might be $[(\text{CN})_4\text{Fe}^{\text{III}}\mu(\text{CN})_2\text{Fe}^{\text{II}}(\text{CN})_3\text{NO}]^{3-}$ while product b might be $[(\text{NO})(\text{CN})_3\text{Fe}^{\text{II}}\mu(\text{CN})_2\text{Fe}^{\text{II}}(\text{CN})_3\text{NO}]^{2-}$. We must emphasise we do not suggest these are the structures; they are merely given to clarify by formulae what we have expressed in words. We have virtually no evidence for the structure of the reaction product of $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{phen})]^-$ and $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bipy})]^-$.

Our overall conclusion is therefore that there is good evidence that the reactions of nitric and nitrous acids with iron(III) cyanide complexes occur through nitrogen dioxide as the active species.

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