Reaction between Hexacyanoferrate(III) Ion and Nitric and Nitrous Acids. Part II.[1] Nature of the Intermediate

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The structure of an intermediate formed by reaction of nitrogen dioxide with hexacyanoferrate(III) ion is deduced to be a bridged binuclear complex, $[Fe_2(CN)_9(NO)_2]^{3-}$, on the basis of stoicheiometric, i.r., and Mössbauer evidence. A linear nitrosyl bridge is suggested. The other products, ammonia, carbon dioxide, and cyanogen all suggest that nitrogen dioxide oxidises a cyanide ligand to cyanate, which subsequently decomposes. The intermediate is formed by a disproportionate reaction between two of the $[Fe(CN)_6]^{3-}$–NO_2 adducts.

In the previous paper[1] we showed that in 6 mol dm^{-3} nitric acid containing some nitrous acid there was a reaction with hexacyanoferrate(III) ion which can be summarised as follows:

$$H^+ + HNO_2 + NO_3^- \underset{\text{fast}}{\rightleftharpoons} H_2O + N_2O_4 \underset{\text{fast}}{\rightleftharpoons} 2NO_2$$

$$\begin{tikzcd} NO_2 + [Fe(CN)_6]^{3-} \arrow[r, "\text{slow}"] & \text{Intermediate} + \tfrac{1}{2}HCN \arrow[d, "\text{slow}"] \\ & \text{Infinity product} \end{tikzcd}$$

Before the details of the mechanism can be discussed it is necessary to know the structure of the intermediate formed.

EXPERIMENTAL

Most of the experimental details have been dealt with in the previous paper.[1] When precipitates were produced by the direct addition of silver(I) nitrate solution to the quenched reaction solution, they formed as a rather sticky material that, after washing and drying, gave poorly resolved *X*-ray powder photographs. Much more satisfactory results were obtained by slowly adding the $AgNO_3$ and intermediate solutions to a large volume of water, with stirring. We also found that, when large amounts of urea were used to quench the reaction solution, the precipitates gave much less satisfactory diffraction photographs than when precipitation was carried out without quenching. Diffraction photographs were taken on a Guinier de-Wolff camera (no. 11) using iron radiation. For the early work, air-dried samples were used, because on drying at 100 °C in an oven a distinct smell of hydrogen cyanide was detected.

I.r. spectra were recorded with KBr-disc and Nujol-mull techniques using a Perkin-Elmer 225 spectrometer for high-resolution work. Attempts to obtain Raman spectra failed because of decomposition in the laser beam. Mössbauer spectra were recorded by the P.C.M.U. section, Harwell. We also used the help of their interpretive service.

Analyses.—Silver analyses were carried out by dissolving a weighed sample in 0·5 mol dm^{-3} potassium cyanide solution, and electrolysing with platinum-gauze electrodes with magnetic stirring. The electrode was washed, dried, and weighed. Carbon and nitrogen analyses were carried out on an F and M 185 analyser, normally used with organic samples. A somewhat higher combustion temperature was used, 1 080 instead of 1 020 °C, and some variations in the combustion catalyst were tried, including addition of vanadium penta-oxide. However the use of standard samples of known composition showed that the technique had limitations, and could be relied on only to give comparisons with known standards; absolute analyses for carbon and nitrogen were probably low. Iron(III) in iron(III) hydroxide was determined by dissolving the precipitate in perchloric acid, adding thiocyanate, and measuring the absorption at 460 nm. Standard solutions of iron were used to calibrate the method. Hexacyanoferrate(II) ion was determined by oxidising to hexacyanoferrate(III), and measuring the absorption at 420 nm.

RESULTS

From the kinetic experiments described in the previous paper, it is possible to find conditions under which $[Fe(CN)_6]^{3-}$ ion is quantitatively converted to the intermediate, and no significant amount of decomposition to the infinity product occurs. When such solutions were treated with urea to destroy the excess of HNO_2, and then with excess of $AgNO_3$, a green-yellow precipitate was obtained. Filtration, and back titration of the excess of silver, showed that there was a 2 : 1 silver : iron ratio based on the original $[Fe(CN)_6{}^{3-}]$. Four separate determinations gave a mean ratio of 1·992 (σ = 0·06). A similar experiment on the infinity product gave a buff precipitate, with a ratio of 1·71 : 1. Attempts to precipitate the intermediate from 6 mol dm^{-3} nitric acid by addition of a range of other metal cations were unsuccessful, and the silver precipitate was the only form in which the intermediate was isolated. Our reaction conditions were chosen to be as similar as possible to those used in a standard procedure for preparing disodium pentacyanonitrosylferrate(2—). The species that we describe as the intermediate and infinity products certainly showed many similarities to authentic $[Fe(CN)_5NO]^{2-}$ ion, but they also showed some distinct differences. We summarise below a number of the properties of these precipitates.

Magnetic Properties.—The $AgNO_3$ intermediate was diamagnetic.

X-Ray Powder Photographs.—The precipitate for the intermediate gave lines (in order of decreasing intensity by visual estimation) with *d* values of *3·009*, 3·101, 3·221, 4·119, 4·157, and *3·710*, together with a number of much weaker lines. Those shown in italics correspond to known lines for silver(I) cyanide. The infinity product could be obtained only as a sticky precipitate, and the dried and powdered material showed no lines other than those due to AgCN. No trace of lines due to $Ag_2[Fe(CN)_5NO]$ was detected in either case.

I.r. Spectra.—Both intermediate and infinity precipitates showed sharp bands in the cyanide and nitrosyl stretching regions, similar to those in authentic $Ag_2[Fe(CN)_5NO]$. Under high resolution (KBr discs) the nitrosyl stretching band was resolved into an intense band at 1 937, with a much weaker band at 1 903 cm^{-1}. The nitrosyl stretch for the infinity precipitate showed a very broad band at 1 940 cm^{-1}.

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[1] Part I, K. M. Davies and G. Stedman, preceding paper.

Samples were precipitated from 6 mol dm^{-3} nitric acid, and must have been contaminated with co-precipitated impurities. Weak bands were observed at other frequencies, but they did not appear in all samples, and their relative intensities were variable. We cannot ascribe them with certainty to our intermediate.

Mössbauer Spectra.—The silver intermediate precipitate gave, at room temperature, a spectrum which on computer analysis corresponded to two types of iron nucleus present in equal amounts with the isomer-shift (i.s.) parameters {relative to $Na_2[Fe(CN)_5NO],2H_2O$}, (*a*) 0·07, (*b*) 0·03 mm s^{-1}, and quadropole splittings (q.s.) (*a*) 1·59, (*b*) 1·77 mm s^{-1}. The infinity precipitate gave a spectrum corresponding to a single type of iron nucleus with an i.s. of 0·07 and a q.s. of 1·64 mm s^{-1}. A low-temperature magnetic-field experiment showed the sign of the electric-field gradient at the nucleus to be opposite in sign in the infinity product to $[Fe(CN)_5NO]^{2-}$ ion.

Analyses.—Analyses for silver on a sample of the air-dried silver intermediate gave 46·3%. Analyses by a similar technique on authentic samples of $Ag_2[Fe(CN)_5NO]$ and $Ag_3[Fe(CN)_6]$ showed that our analyses were *ca.* 1% low. The cause of this is not known. Analyses for carbon and nitrogen by standard microanalytical procedures met with many difficulties, presumably due to the formation of carbides and nitrides {Found (4 analyses): C, 12·8 ± 0·4; N, 18·3 ± 0·7. $Ag_2[Fe(CN)_5NO]$ requires C, 13·9; N, 19·4. Found (6 analyses) for silver intermediate: C, 11·2 ± 1·6; N, 18·0 ± 0·7. Found (15 analyses) for silver infinity product: C, 11·4 ± 1·3; N, 18·3 ± 0·7%}. The errors quoted are standard deviations.

Properties of the Intermediate in Solution.—The feature of the intermediate in solution which distinguished it most clearly from authentic $[Fe(CN)_5NO]^{2-}$ ion and from the infinity product was its u.v. absorption spectrum. The intermediate was characterised by a broad maximum at 382 nm {ε 960 dm^3 mol^{-1} cm^{-1}, based on the original $[Fe(CN)_6{}^{3-}]$}, whereas the infinity product showed negligible absorption in this region. The ion $[Fe(CN)_5NO]^{2-}$ has a peak at 395 nm (ε 21 dm^3 mol^{-1} cm^{-1}). In most other respects measurements on solutions of the intermediate gave results very similar to those obtained with authentic $[Fe(CN)_5NO]^{2-}$ ion. The significant experiments are described below.

Solutions of $[Fe(CN)_5NO]^{2-}$ ion when treated with excess of alkali and potassium cyanide, so that final concentrations were $[OH^-] = 0{\cdot}4$ and $[CN^-] = 0{\cdot}2$ mol dm^{-3}, underwent reaction (1). Experiments with the intermediate showed

$$CN^- + [Fe(CN)_5NO]^{2-} + 2OH^- \longrightarrow [Fe(CN)_6]^{4-} + NO_2^- + H_2O \qquad (1)$$

its similarity to $[Fe(CN)_5NO]^{2-}$, one mole of nitrite ion and one mole of $[Fe(CN)_6]^{4-}$ being formed per mole of original $[Fe(CN)_6]^{3-}$. A similar result was obtained for the infinity product. In the absence of cyanide ion $[Fe(CN)_5NO]^{2-}$ and alkali reacted to form bright yellow $[Fe(CN)_5NO_2]^{4-}$, the rate law[2] being $v = k[Fe(CN)_5NO^{2-}][OH^-]$.

$$[Fe(CN)_5NO]^{2-} + OH^- \xrightarrow[\text{slow}]{k} [Fe(CN)_5(NO_2H)]^{3-} \xrightarrow[\text{fast}]{OH^-} [Fe(CN)_5NO_2]^{4-} \qquad (2)$$

The intermediate behaved similarly. In alkali a yellow complex was formed, ε_{400} 2 600 dm^3 mol^{-1} cm^{-1}. {For $[Fe(CN)_5NO_2]^{4-}$ under our conditions we found ε_{400} 3 220 dm^3 mol^{-1} cm^{-1}; Swinehart and Rock reported ε_{400} to be 3 075 dm^3 mol^{-1} cm^{-1}.} The rate constant k for the intermediate was 0·149 compared to 0·285 dm^3 mol^{-1} s^{-1} for $[Fe(CN)_5NO]^{2-}$ ion under our conditions, $I = 0{\cdot}3$ mol dm^{-3} and 25 °C. Individual runs with a large excess of hydroxide gave excellent pseudo-first-order plots over at least three half-lives. A marked difference between the intermediate and $[Fe(CN)_5NO]^{2-}$ ion showed up when the reaction was followed for longer periods of time. Although $Fe[(CN)_5NO_2]^{4-}$ underwent slow hydrolysis through dissociation of the nitrite ion and formation of $[Fe(CN)_5H_2O]^{3-}$, in the presence of excess of nitrite ion in solution this dissociation was supressed and the yellow solution was stable. In some experiments we could detect no change over 36 h. Solutions of the intermediate in alkali, with excess of nitrite ion, were much less stable. A cloudiness appeared in the solution shortly after formation of the yellow colour was complete, and on standing the yellow colour faded and a reddish brown precipitate of iron(III) hydroxide appeared. Reaction was complete within 24 h at room temperature. The other product identified was $[Fe(CN)_6]^{4-}$. The results are summarised below where $[\text{Intermediate}]_0$ represents the initial intermediate concentration {based on the initial $[Fe(CN)_6{}^{3-}]$}. The main problems in the $Fe(OH)_3$ analysis arose from its colloidal nature, and we doubt if the analyses are better than ±5%. In most cases our analyses account for over 80% of the original $[Fe(CN)_6]^{3-}$ ion and our best result accounts for 97·6%. A similar experiment carried out on the infinity solution yielded 43% $Fe(OH)_3$ and 57% $[Fe(CN)_6]^{4-}$.

Products of decomposition of the intermediate in alkali

$10^4\,[\text{Intermediate}]_0$ / mol dm^{-3}	$10^3[NO_2^-]$ / mol dm^{-3}	% $Fe(OH)_3$	% $[Fe(CN)_6]^{4-}$
2	5	41·2	45·5
4	10	41·0	44·0
8	20	47·0	50·6
16	40	17·9	64·5
16[a]	40	21·0	65·0
32	80	12·9	53·7

[a] $[OH^-] = 0{\cdot}08$ mol dm^{-3}; in all other experiments $[OH^-] = 0{\cdot}4$ mol dm^{-3}.

In an attempt to obtain information about the charge on the intermediate, the relative rates of uptake of the intermediate and $[Fe(CN)_6]^{3-}$ ion on to an anion-exchange resin, Amberlite I.R.A. 400 in the nitrate form, were measured. Solutions containing both $[Fe(CN)_6]^{3-}$ ion and the intermediate were shaken with the resin, and their disappearance calculated from absorbance measurements at the maxima at 420 and 380 nm respectively. Measurements were made over a short enough period that decomposition of the intermediate to the infinity product could be neglected. The rates of uptake were similar, that of $[Fe(CN)_6]^{3-}$ ion being slightly faster. Attempts to obtain the same information by studying rates of elution from an ion-exchange resin were unsuccessful because of decomposition of the intermediate to the infinity product.

DISCUSSION

We shall begin by discussing the structures of the intermediate and infinity products. When these are established, at least tentatively, we shall attempt to interpret the kinetic results described in the previous paper. It is clear that although we have deliberately used conditions

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[2] J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, 1966, **5**, 573.

as close as possible to those of Brauer's preparative method, neither our intermediate nor our final product is [Fe(CN)$_5$NO]$^{2-}$. The u.v. spectrum of the intermediate in solution is different, and the colours of the silver precipitates differ from that of authentic Ag$_2$[Fe(CN)$_5$NO] precipitated under identical conditions, and, more damning, the *X*-ray powder-diffraction photographs are different. Thus, although there are undoubtedly many similarities to [Fe(CN)$_5$NO]$^{2-}$, we are looking for two different species. The i.r. spectra clearly show the presence of an NO$^+$ ligand in both intermediate and infinity products. This is confirmed by the fact that treatment with alkali and cyanide releases one mole of nitrite per mole of original [Fe(CN)$_6$]$^{3-}$ ion. The similarity in the spectra of the yellow species formed on treating the intermediate and [Fe(CN)$_5$NO]$^{2-}$ ion with alkali, and the similarity in the rates at which these species are formed argues in the same direction. The fact that reaction of the intermediate with alkali and cyanide gives a quantitative yield of [Fe(CN)$_6$]$^{4-}$ ion shows that we have a species with iron in the oxidation state II. This is also consistent with the silver salt being diamagnetic. The Mössbauer spectra of the silver salt of the infinity product show that this too is diamagnetic, and presumably iron(II). The i.s.'s observed in the Mössbauer spectra are in the range known for iron(II) compounds, though this is not a very conclusive piece of information as the ranges for iron-(II) and -(III) overlap.[3]

The stoicheiometric determinations show that when the intermediate is precipitated as its silver salt, two moles of silver ion are consumed per mole of original [Fe(CN)$_6$]$^{3-}$. When precipitation takes place 0·5 mole of hydrogen cyanide is released per mole of [Fe(CN)$_6$]$^{3-}$ ion, and blank experiments showed that this should be quantitatively precipitated in 6 mol dm^{-3} nitric acid, even though the pK_a is 10. The *X*-ray powder photograph shows the characteristic line for AgCN. Hence it would appear that 1·5 moles of silver are used in precipitating the intermediate. The most valuable piece of information on the structure of the intermediate comes from Mössbauer spectra, which show that the silver intermediate contains two types of iron nucleus in a 1 : 1 ratio. The i.s. and q.s. values are similar to those for authentic Ag$_2$[Fe(CN)$_5$NO]. This suggests that either we have precipitated two different compounds of iron(II), or that we have an unsymmetrical binuclear complex. The fact that the yield of HCN is *ca.* 50% when formation of the intermediate is complete suggests that there are two different types of iron present in equal amounts. The fact that there seems to be a limiting yield of 50% Fe(OH)$_3$ and 50% [Fe(CN)$_6$]$^{4-}$ in the decomposition of the intermediate in alkali points in the same direction. Attempts to separate the intermediate into fractions by partial precipitation with AgNO$_3$ were unsuccessful, though this could be due to a failure in our technique; thus we were not able to separate the cyanide from the intermediate either. A very successful method for separating cyanide complexes and determining the approximate molecular weight is by passage through a Sephadex column. However, the instability of the intermediate rendered experiments of this type inconclusive. We did not find evidence at any stage for fractionation of the intermediate into two compounds. A final argument is that we are quite unable to suggest two species, both similar to but different from [Fe(CN)$_5$NO]$^{2-}$, that could decompose by a first-order reaction to give another product again similar to, but different from, [Fe(CN)$_5$NO]$^{2-}$.

We are forced to the conclusion that our intermediate is a binuclear species. The fact that the silver to iron ratio is 3 : 2 suggests a charge of 3$-$. This is consistent with the results of the ion-exchange experiment, though experiments were not carried out with a wide enough range of anions to make this a strong piece of evidence on its own. As there is one nitrosyl ligand per atom of iron, a formal balancing of charges requires there to be nine cyanide ligands. With 11 ligands in all, this must be a singly bridged complex [Fe$_2$(CN)$_9$(NO)$_2$]$^{3-}$ with either a bridging cyanide or nitrosyl group. I.r. spectroscopy would seem the obvious method of distinguishing between two possibilities. A good deal of work has been done on the i.r. spectra of linear cyanide bridges, and it has been reported that they are characterised by a band *ca.* 100 cm^{-1} higher than the normal cyanide stretching.[4] A similar result has been found[5] for [Fe$_2$(CN)$_{10}$]$^{4-}$, which appears to be a doubly bridged species where the cyanide bridges cannot be linear. We have not found any such band in our spectra. Not very much is known about bridging nitrosyl groups. Those that are known bridge in a non-linear manner through the nitrogen atom and have[6] i.r. bands in the range 1 330—1 550 cm^{-1}, very much lower than in our spectra. Linear nitrosyl bridges do not seem to have been reported. Another ligand isoelectronic to the nitrosonium ion is dinitrogen. A substantial number of complexes with this ligand have been made, and it appears that a binuclear complex with a linear $-N{\equiv}N-$ bridge shows a *lower* frequency for the N≡N vibration than the analogous mononuclear species. For the salt [Ru(NH$_3$)$_5$(N$_2$)](BF$_4$)$_2$ the band is at 2 154 compared with 2 100 cm^{-1} for [(NH$_3$)$_5$Ru$-$N≡N$-$Ru(NH$_3$)$_5$](BF$_4$)$_4$. Several other examples could be quoted,[7–9] all of which show a *reduction* in frequency in the species with a dinitrogen bridge. The fact that the isoelectronic species cyanide ion and dinitrogen show respectively an increase and a decrease in vibrational frequency on forming a bridge is striking, and is doubtless to be interpreted in terms of the relative contributions of σ-donor and π-acceptor bonding. We suggest that the weak band at 1 903 cm^{-1} in our intermediate is due to a linear

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[3] N. Greenwood and T. C. Gibb, ' Mössbauer Spectroscopy,' Chapman Hall, London, 1971, p. 91.

[4] A. Haim, D. A. Dows, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

[5] R. S. Murray, personal communication.

[6] J. E. Huheey, ' Inorganic Chemistry, Principles of Structure and Reactivity,' Harper and Row, London, 1972, p. 459.

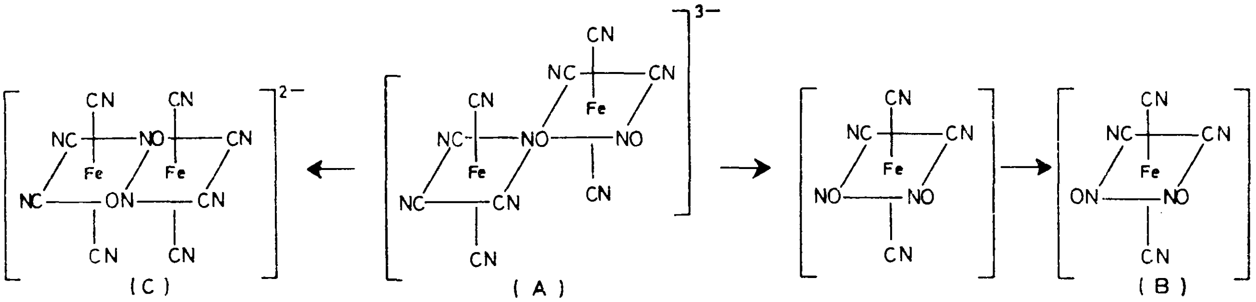
[7] A. D. Allen and C. V. Senoff, *Chem. Comm.*, 1965, 621.

[8] J. Chatt and G. J. Leigh, *Chem. Soc. Rev.*, 1972, **1**, 121.

[9] M. N. Hughes, ' The Inorganic Chemistry of Biological Systems,' Wiley, London, 1962, p. 210.

Fe–N≡O–Fe bridge, while the other peak at 1 940 cm^{-1} is due to a terminal linear nitrosyl group, similar to that in $[Fe(CN)_5NO]^{2-}$ ion.

Another piece of evidence leading to the same conclusion concerns the structure of the infinity product formed by first-order decay of the intermediate. The Mössbauer spectrum shows it to contain a single type of iron nucleus, in an environment very similar to authentic $[Fe(CN)_5NO]^{2-}$ ion. However, the low-temperature magnetic-field Mössbauer spectrum shows the sign of the electric-field gradient at the nucleus to be opposite to that of $[Fe(CN)_5NO]^{2-}$ ion. Simple theory indicates that the presence of a structure with *cis*-nitrosyl groups. We can only find two structures that satisfy the requirements of the Mössbauer spectrum, (B) and (C). Either of these could be visualised as being readily formed from a nitrosyl-bridged structure. To form these structures from a cyanide-bridged structure would require a much more complex rearrangement. Several lines of evidence favour (C), but our work on the infinity product is not yet complete and we will present the evidence later. The choice between (B) and (C) does not affect the present argument. Structure (A) is clearly consistent with our Mössbauer evidence. The magnitude of the q.s. is the same in FeX_5Y as it is in *cis*-FeX_4Y_2, and does not depend on the sign of the electric-field gradient. Thus both iron nuclei in (A) will have $[Fe(CN)_5NO]^{2-}$-like environments, with similar q.s. and i.s. values, as is observed. The most dubious feature of this argument is the tacit assumption that the nitrosyl ligand has the same effect on the iron nucleus whether it is bonded through nitrogen or oxygen. This is unlikely to be strictly true, but we cannot make any other assumption at this stage. It is clear that the non-bridging nitrosyl group in (A) must be *cis* to the bridging nitrosyl; if it were *trans* then one of the iron nuclei would show a q.s. half that of $[Fe(CN)_5NO]^{2-}$, as theory predicts for *trans*-FeX_4Y_2 compared to FeX_5Y. It is also probable that there will be an effect because the nitrosyl bridges in (C) must be non-linear. It would be interesting to look at the Mössbauer spectra of the known dimer $[Fe_2(CN)_{10}]^{6-}$ and compare it with $[Fe(CN)_6]^{4-}$ ion.



It would be very desirable to confirm this structure by analytical data on the precipitated solid. Our solid is suggested to be $Ag_3[Fe_2(CN)_9(NO)_2]$ + AgCN. This has the same overall composition as $Ag_2[Fe(CN)_5NO]$, and should give identical analyses. The figure for silver was 46·4%, compared with a theoretical value of 50·0%. Analysis of standard substances gave figures that were 1% low. Even assuming that this can be applied to our silver intermediate precipitate the analysis is still 3% low. There were many problems in the microanalytical determination of nitrogen and carbon, and we were forced to rely on comparison with known standards, rather than use the absolute figures. As the intermediate shows many similarities to $[Fe(CN)_5NO]^{2-}$ ion, and by good fortune is thought to have the same overall composition, we used $Ag_2[Fe(CN)_5NO]$ as our standard. Carbon and nitrogen analyses for the intermediate and $[Fe(CN)_5NO]^{2-}$ agreed within the rather large standard deviations, and the same is true for the infinity product. The data are consistent with our postulated composition, but are not good enough to prove it.

The general similarity between $[Fe(CN)_5NO]^{2-}$ ion and our intermediate seems reasonable in the light of structure (A). Reaction with alkali presumably involves conversion of the non-bridging nitrosyl to a nitro-group initially. The rate constant was similar to that observed for the corresponding $[Fe(CN)_5NO]^{2-}$ reaction; the fact that it is close to half the value is probably a coincidence. If the product $[(NC)_5Fe\text{–}NO\text{–}Fe(CN)_4NO_2]^{5-}$ broke down rapidly then we would expect release of $[Fe(CN)_5NO]^{2-}$ which would react with alkali at a rate similar to that of the intermediate to form the ion $[Fe(CN)_5NO_2]^{4-}$. We would certainly not expect the simple first-order kinetics observed under these conditions. It seems much more probable that the slow reaction actually observed, which leads to formation of $[Fe(CN)_6]^{4-}$ ion and $Fe(OH)_3$ overnight, arises from slow breakdown to $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_4(H_2O)NO_2]^{3-}$. Presumably it is the latter species that overnight hydrolyses to yield $Fe(OH)_2$ [oxidised by dissolved dioxygen to $Fe(OH)_3$] and cyanide ion. The ion $[Fe(CN)_5NO]^{2-}$ in alkali and cyanide gives $[Fe(CN)_6]^{4-}$ quantitatively, so the limiting yields should be 50% $[Fe(CN)_6]^{4-}$ and 50% $Fe(OH)_3$. Our results approach this at low initial intermediate concentrations, and in the case where we have a 97·6% material the yields were close to these limits. In the presence of excess of cyanide ion produced by hydrolysis it may be that there is some reaction (3).

$$2CN^- + [Fe(CN)_4(H_2O)NO_2]^{3-} \longrightarrow [Fe(CN)_6]^{4-} + NO_2^- + H_2O \quad (3)$$

Presumably this is why the $[Fe(CN)_6]^{4-}$ yield is often greater than 50%. It is significant that the experiments with the highest initial intermediate concentration, which will produce the highest cyanide concentration by hydrolysis, also produce the lowest yields of $Fe(OH)_3$ and the highest yields of $[Fe(CN)_6]^{4-}$. The limiting yield, when all the cyanide ion is used in this way, will correspond to a $[Fe(CN)_6]^{4-}$ yield of $100 \times (10/12) = 83{\cdot}3\%$. The highest figure we obtained was 65%.

The kinetics, discussed in the previous paper, showed that the intermediate was formed by a reaction of nitrogen dioxide with $[Fe(CN)_6]^{3-}$ ion. In the process an atom of iron(III) is reduced to iron(II), and a nitrosyl cation is introduced as a ligand. Simple material balance shows an atom of oxygen still to be accounted for. The reaction products include ammonia, carbon dioxide, and cyanogen. This suggests that a cyanide ion is oxidised to cyanate (or fulminate). Acid hydrolysis of cyanic acid is known to produce ammonia and carbon dioxide, very rapidly, and cyanogen is the pseudo-halogen derived from cyanic acid and hydrogen cyanide. We cannot account quantitatively for all cyanide which we postulate to be oxidised to cyanate; the final yield of ammonia is 50% of the maximum possible value.

The intermediate, being a binuclear complex, must be derived from two species formed by initial reaction between NO_2 and $[Fe(CN)_6]^{3-}$ ion. We call this species the ' monomer.' The close agreement between the rate of disappearance of $[Fe(CN)_6]^{3-}$ ion and the rate of appearance of the intermediate shows that this ' dimerisation ' must be a rapid process; there does not seem to be any build-up of the ' monomer.' This is confirmed by the observation of an isosbestic point in the u.v. spectra, when the $[Fe(CN)_6]^{3-}$ peak at 420 nm was being replaced by the intermediate peak at 382 nm. Discussion of the nature of the ' monomer ' is more speculative. It seems improbable that the cyanate ion is released from the ' monomer '; if it is there seems no obvious reason why the monomer should not be the ion $[Fe(CN)_5NO]^{2-}$. A possible alternative would be an isomer, a nitrosyl-*O*-complex as in equations (4)—(6). This assumes that

$$NO_2 + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_5ON]^{2-} + OCN^- \qquad (4)$$

$$2[Fe(CN)_5ON]^{2-} \longrightarrow [(NC)_5Fe{-}ON{-}Fe(CN)_4ON]^{3-} + CN^- \qquad (5)$$

$$\downarrow$$

$$[(NC)_5Fe{-}ON{-}Fe(CN)_4NO]^{3-} \qquad (6)$$

' dimerisation ' occurs before the nitrosyl-*O* group has a chance to isomerise to the normal nitrogen-bonded form. Isomerisation of nitrogen-bonded cyanide to the more-stable carbon-bonded form can occur sufficiently slowly to be followed kinetically.[10] It is, however, surprising if a cyanide ion could be displaced sufficiently rapidly in (5) to occur faster than isomerisation. Possibly a more cogent objection is the fact that the yield of ammonia is 50%. This suggests that the two cyanate groups have different fates. The 50% yield could be a chance result, or it might be due to some disproportionation reaction of cyanate. Adamson,[11] in studying alkaline oxidation of cyanide by $[Fe(CN)_6]^{3-}$ ion, could only account for 50% of his product as ammonia.

If the cyanate ion is still attached to the monomer, then it is probably bound to the nitrogen atom of the nitrosyl group. The ion $[Fe(CN)_5NO]^{2-}$ forms adducts with many species, which are written as $[Fe(CN)_5(NOX)]^{2-}$ where X is the species in question. Some of these systems have been studied, in detail, and the structures suggested are of the type $-N(O)X$. Swinehart[12] and Lancaster and Murray[13] have suggested that, in the oxidation of sulphite by $[Fe(CN)_6]^{3-}$ ion, sulphite adds on in a similar fashion to a cyanide ion, producing a species $[Fe(CN)_5(CNSO_3)]^{5-}$, analogous to the well known adduct of SO_3^{2-} and $[Fe(CN)_5NO]^2$. If such an addition were to occur in our system, the bonding of a cyanate onto a cyanide ion might appear to provide a route for formation of cyanogen. However, we can account for all the cyanide except that postulated to be oxidised to cyanate, so such a reaction cannot be of any importance. Thus we suggest a structure of the type $[(NC)_5Fe{-}N(O)OCN]^{3-}$. We also suggest that the two cyanates are lost in separate stages, and may suffer different fates.

$$2[(NC)_5Fe\{N(O)OCN\}]^{3-} \longrightarrow [(NC)_5Fe{-}NO{-}Fe(CN)_4\{N(O)OCN\}]^{4-} + OCN^- + CN^- \qquad (7)$$

$$\downarrow$$

$$[(NC)_5Fe{-}NO{-}Fe(CN)_4NO]^{3-} + OCN^- \qquad (8)$$

In view of the variety of functions that NO_2 has performed in this reaction, reducing iron-(III) to -(II), oxidising cyanide ion to the level of cyanate, and introducing a nitrosyl ligand into the co-ordination shell, it would be interesting to examine the reactions of nitric and nitrous acids with other metal complexes.

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