Reaction between Hexacyanoferrate(III) Ion and Nitric and Nitrous Acids. Part I. Kinetics

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Hexacyanoferrate(III) ion, $[Fe(CN)_6]^{3-}$, reacts with 6 mol dm^{-3} nitric acid, in the presence of nitrous acid, to form an iron cyanonitrosyl complex according to the rate law $v = k[Fe(CN)_6{}^{3-}][HNO_2]^{\frac{1}{2}}$. The reaction has been carried out in sulphuric acid, with low concentrations of nitric and nitrous acids, and k varies with $h_-{}^{\frac{1}{2}}$, an acidity function for ionisation of HNO_3, and $[HNO_3]^{\frac{1}{2}}$. Reaction occurs by attack of an equilibrium concentration of nitrogen dioxide on $[Fe(CN)_6]^{3-}$ ion. The intermediate species so formed undergoes a further slow reaction, following first-order kinetics.

ALTHOUGH the structure, bonding, and properties of transition-metal nitrosyl complexes have been widely studied, there has been relatively little work on the kinetics and mechanism of their formation in solution. Studies of the conversion of hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$, to pentacyanonitrosylferrate(2−) ion,

$[Fe(CN)_5NO]^{2-}$, at pH values greater than 7 have been reported,[1] and this reaction proceeds through slow ligand replacement involving nitrite ion. Standard preparative methods [2] involve digesting tripotassium hexacyanoferrate(III) or tetrapotassium hexacyanoferrate(II) with moderately concentrated nitric acid (30% w/w) at *ca.* 45 °C for 1—2 d. We have investigated the kinetics of the reaction under conditions as similar as possible to these, though a few differences were forced upon us; lower concentrations of $[Fe(CN)_6]^{3-}$ ion were used as those in the preparative method were far too high for kinetic work. It is clear that nitrous acid is involved in the reaction, so we chose to add a known amount of nitrite initially to the system rather than rely on the variable amount present in nitric acid. Because of the thermal instability of nitrous acid, we worked at 25 rather than 45 °C. Hexacyanoferrate(III) rather than hexacyanoferrate(II) ion was used because of the greater stability of aqueous solutions of the former, although in the presence of nitric and nitrous acids a redox equilibrium is set up and both species will be present. We were also interested in the reaction because it formally involves replacement of a cyanide ion ligand by a nitrosonium ion, a species which normally functions as an electrophile.

EXPERIMENTAL

All chemicals were AnalaR materials and were used without further purification. Solutions of tripotassium hexacyanoferrate(III), tetrapotassium hexacyanoferrate(II), and disodium pentacyanonitrosylferrate(2−) were kept in black painted bottles to avoid photochemical effects. Freshly prepared solutions were used in all experiments.

Analyses.—Nitrous acid was determined by a standard colorimetric method,[3] absorbance measurements being made immediately after coupling the diazonium ion. Hexacyanoferrate(III) ion was determined by destroying nitrous acid with urea or sulphamic acid, diluting the sample with water to *ca.* 0·6 mol dm^{-3} acid, removing dissolved dioxygen by bubbling dinitrogen through the solution, and adding potassium iodide. $ZnSO_4$ Was added to force the $[Fe(CN)_6]^{3-}$, I^-–$[Fe(CN)_6]^{4-}$, I_2 equilibrium in favour of iodine which was then titrated with disodium thiosulphate. Silver(I) ion was determined by titration with bromide, using Rhodamine 6G as indicator. Some silver analyses were carried out electrolytically. Pentacyanonitrosylferrate(2−) ion was estimated by treatment with 0·2 mol dm^{-3} potassium cyanide–0·5 mol dm^{-3} alkali. Under these conditions nitrite ion is released quantitatively. After acidification, the nitrite was determined by the normal colorimetric method involving diazotisation of sulphanilic acid, and coupling of the resulting diazonium ion. This method can be used to determine cationic nitrosyl ligands in complexes similar to $[Fe(CN)_5NO]^{2-}$, and we found it possible to determine the intermediate species in the present reaction by this method, and also the infinity product formed by decay of the intermediate. Both these species showed many similarities to $[Fe(CN)_5NO]^{2-}$ in their reactions. We used this reaction as an analytical method to determine the *initial* rate of formation of our intermediate. We knew from spectrophotometric evidence that the decay of the intermediate to the infinity product was very much slower than its formation. Thus in the first few minutes of reaction it was possible to determine the intermediate without interference from the infinity product. Hexacyanoferrate(III) ion interfered slightly with this method, probably by oxidation of $[Fe(CN)_5NO_2]^{4-}$ formed by $[Fe(CN)_5NO]^{2-}$ in alkali.

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

Ammonia was determined by precipitating all the iron species in solution with excess silver(I) nitrate, centrifuging, and precipitating the excess of silver with sodium chloride. The solution was then made alkaline, and the ammonia determined by distillation into a known excess of hydrochloric acid, followed by back titration. Attempts to observe the characteristic ^1H n.m.r. spectrum of the ammonium ion in the reaction solution were unsuccessful, due to overlap with the solvent peak. Analysis for hydrogen cyanide in the presence of the various cyanide complexes presented problems. Finally we adopted the procedure of quenching reaction solutions with urea, and extracting the hydrogen cyanide with di-isopropyl ether. From this, the cyanide was re-extracted into aqueous solution and determined colorimetrically.[4] The method was calibrated with known cyanide solutions. Gas evolution was followed by a standard Warburg method.

Kinetics.—Spectrophotometric measurements were made on a Unicam SP 500 instrument, fitted with a constant-temperature jacket for the cells. Recorded spectra were obtained on a Unicam SP 800 instrument. Runs followed by chemical analysis were carried out in flasks, painted black on the outside, and screened from direct light. A surface layer of hexane was used to reduce the self decomposition of nitrous acid.

RESULTS

Solutions of potassium hexacyanoferrate(III) in 6 mol dm^{-3} nitric acid were quite stable when the last traces of nitrous acid were removed by added sulphamic acid or urea. In the presence of nitrous acid reaction occurred, the main features of which were shown very clearly by changes in the visible and u.v. spectra. On mixing the reactants there was a rapid decrease in absorbance of the characteristic $[Fe(CN)_6]^{3-}$ peak at 420 nm, complete in 1—2 min. The magnitude of this decrease varied somewhat with conditions, but on average was *ca.* 25% of the initial absorbance. There was no change in the shape of the peak. The initial decrease was followed by a second stage in which the 420 nm peak disappeared and was replaced by a new peak at 382 nm, with an isosbestic point at *ca.* 398 nm (the exact wavelength varied slightly with reaction conditions). This second stage took the order of 10—15 min to go to completion. The final change was a slow disappearance of the 382 nm peak over a period of several hours. A typical series of spectra showing the first two changes is shown in Figure 1. Measurements at a single wavelength (Figure 2) show the three stages (*i*)—(*iii*) quite clearly. The species absorbing at 382 nm, and formed in stage (*ii*), we call the intermediate. The structure of the latter is discussed in the following paper, and here we note that it is a diamagnetic iron cyanonitrosyl

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[1] V. Schwarzkopf, *Lotas. Prag.*, 1911, **3**, 1; F. Seel and H. Koss, *Z. Naturforsch.*, 1962, **B17**, 129.

[2] G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' Academic Press, 1965, vol. 2, p. 1768.

[3] C. A. Bunton, E. A. Halevi, and D. R. Llewellyn, *J. Chem. Soc.*, 1952, 4913.

[4] F. B. Fisher and J. S. Brown, *Analyt. Chem.*, 1952, **24**, 1440.

complex, containing one NO^+ ligand per atom of iron, and is similar in many of its reactions to $[Fe(CN)_5NO]^{2-}$.

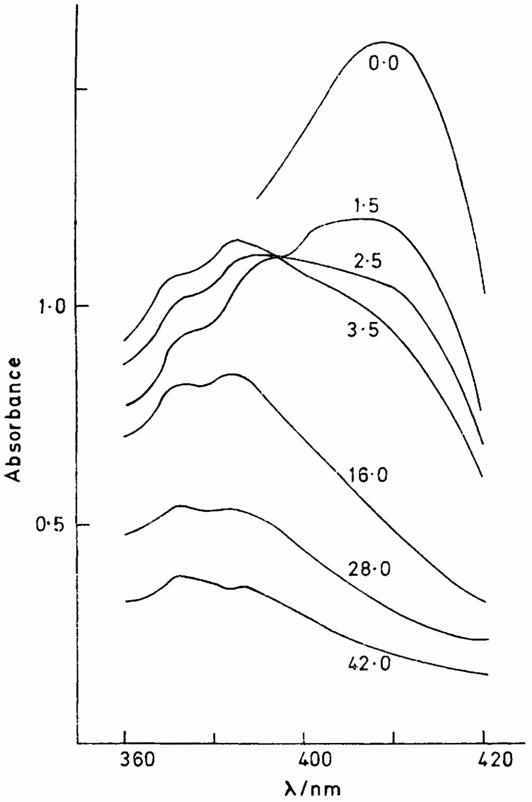

FIGURE 1 Variation of absorption spectrum of the reaction mixture with time: $[HNO_3] = 6$; $[Fe(CN)_6{}^{3-}]_0 = 0{\cdot}016$; and $[HNO_2]_0 = 0{\cdot}04$ mol dm^{-3}. Numbers on the curves represent time in minutes

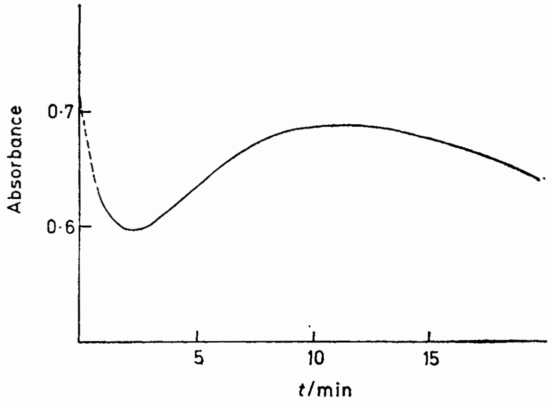

FIGURE 2 Variation of absorbance at 392 nm as a function of time: $[HNO_3] = 6$; $[Fe(CN)_6{}^{3-}]_0 = 0{\cdot}008$; and $[HNO_2]_0 = 0{\cdot}04$ mol dm^{-3}

It may be helpful to outline at this stage the main features of the mechanism that is finally proposed. Stage (*i*) is associated with the rapid establishment of equilibrium (2);

$$2[Fe(CN)_6]^{3-} + HNO_2 + 2H^+ + H_2O \rightleftharpoons 2[Fe(CN)_6(H)_2]^{2-} + HNO_3 \quad (2)$$

stage (*ii*) is attack by an equilibrium concentration of nitrogen dioxide on $[Fe(CN)_6]^{3-}$ ion; and stage (*iii*) is slow conversion of the intermediate to an infinity product.

$$H^+ + HNO_2 + NO_3^- \overset{K_1}{\rightleftharpoons} N_2O_4 + H_2O, \text{ fast} \quad (3)$$

$$N_2O_4 \overset{K_7}{\rightleftharpoons} 2NO_2, \text{ fast} \quad (4)$$

$$NO_2 + [Fe(CN)_6]^{3-} \longrightarrow \text{Intermediate} + \tfrac{1}{2}HCN, \text{ slow} \quad (5)$$

Aliquot portions of reaction mixture were taken at various times and urea added to quench the reaction by destroying the nitrous acid. Silver(I) nitrate was then added and the resulting precipitate washed and dried. During stages (*i*) and (*ii*) the precipitate had the characteristic orange-red colour of trisilver hexacyanoferrate(III), and the i.r. spectrum (Nujol mull) showed a strong sharp peak at 2 170 cm^{-1}, a strong and broader peak at 1 940 cm^{-1}, and a weak broad band at 2 040 cm^{-1}. The relative intensity of the bands at 1 940 and 2 170 cm^{-1} increased with time during stage (*ii*). Samples precipitated when stage (*ii*) was complete were yellow-green and showed peaks at 2 170 and 1 940 cm^{-1}; the peak at 2 040 cm^{-1} had disappeared. Samples precipitated at the end of stage (*iii*) were grey, and gave similar peaks at 2 170 and 1 940 cm^{-1}. For purposes of comparison we ran i.r. spectra of several related complexes. Trisilver hexacyanoferrate(III) showed a sharp peak at 2 172 cm^{-1}, disilver pentacyanonitrosylferrate(2−) a sharp peak at 2 178 cm^{-1} and strong peak at 1 940 cm^{-1}. Tetrasilver hexacyanoferrate(II) showed a broad peak at 2 040 cm^{-1}. The peaks at 2 040 and 2 170 cm^{-1} are assigned to the triple-bond stretching frequencies of the cyanide ligand; that at 1 940 cm^{-1} is the stretching frequency for a co-ordinated nitrosyl group.

Stoicheiometry.—The i.r. results summarised above clearly show that $[Fe(CN)_6]^{4-}$ ion is formed during stage (*i*) of the reaction. This is due to the establishment of equilibrium (2). We studied this equilibrium in detail by spectrophotometric and e.m.f. methods in perchloric and sulphuric acids, as described in a previous paper.[5] As discussed in the final section of this paper, we suspect that the initial reaction may be more complex than this.

We determined the stoicheiometry for stage (*ii*) by allowing an excess of $[Fe(CN)_6]^{3-}$ ion to react completely with nitrous acid, and then measuring the residual $[Fe(CN)_6]^{3-}$. Typical results are:

$10^3[HNO_2]_0$/mol dm^{-3}	1·6	1·2	0·8	0·4
R	2·00	2·04	2·03	2·10

$10^3[Fe(CN)_6{}^{3-}]_0$/mol dm^{-3} = 8·0

where $R = \{[Fe(CN)_6{}^{3-}]_0 - [Fe(CN)_6{}^{3-}]_\infty\}/[HNO_2]_0$

We also carried out runs in which both $[Fe(CN)_6]^{3-}$ and HNO_2 concentrations were followed as a function of time, and these too gave $\Delta[Fe(CN)_6{}^{3-}]/\Delta[HNO_2] = 2$. This was confirmed by kinetic studies described below where the rate constant for loss of $[Fe(CN)_6]^{3-}$ ion was slightly more than twice that for loss of nitrous acid, although the form of the rate laws was identical. Runs in which the disappearance of $[Fe(CN)_6]^{3-}$ ion and the appearance of the intermediate were followed showed that one mole of co-ordinated nitrosyl group (in the intermediate) was formed per mole of original $[Fe(CN)_6]^{3-}$. Analysis of the intermediate showed that one mole of nitrous acid gave rise to two moles of co-ordinated nitrosyl groups in the intermediate, providing further confirmation of the 2 : 1 stoicheiometry. We have no evidence

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[5] J. C. Bates, K. M. Davies, and G. Stedman, *J.C.S. Dalton*, **1974**, 246.

for the amount of nitric acid consumed, but we observed hydrogen cyanide as a product of stage (*ii*); the yield was 0·48 mole per mole of original $[Fe(CN)_6]^{3-}$. There was a further slow release of hydrogen cyanide during stage (*iii*), and the final yield was 0·68 mole per mole of original $[Fe(CN)_6]^{3-}$. Ammonia was also a product; relatively little was released during stage (*ii*), but by the end of stage (*iii*) we found 0·48 mole per mole of original $[Fe(CN)_6]^{3-}$. In two runs we followed the increase in hydrogen cyanide and ammonia concentrations respectively as a function of time. The concentrations increased smoothly with time, and showed no sign of any induction period, or any unusual variation within the first few minutes of reaction, *i.e.* during stage (*i*). Experiments with a Warburg apparatus showed 0·5 moles of gas to be evolved, and mass-spectrometric analysis established the presence of carbon dioxide and cyanogen.

Kinetics.—Three chemical methods were used to follow the kinetics of reaction (*ii*).

$[Fe(CN)_6]^{3-}$ *Analysis.* Runs were carried out with a large excess of HNO_2 over $[Fe(CN)_6]^{3-}$ ion. Individual runs gave good first-order plots over at least two, and often three, half-lives, extrapolating to the expected initial $[Fe(CN)_6]^{3-}$ concentrations at zero time. There were no signs of any deviations in the first few minutes of reaction. Pseudo-first-order rate constants are given in Table 1. The results fit the rate law (6) at 25 °C. The temperature variation of

TABLE 1

Rate constants for the disappearance of hexacyanoferrate(III) ion in 6 mol dm^{-3} nitric acid at 25 °C

$[Fe(CN)_6{}^{3-}]$ / mol dm^{-3}	$[HNO_2]$ / mol dm^{-3}	10^3k_1 / s^{-1}	10^2k_2 / mol$^{-\frac{1}{2}}$ dm$^{-3/2}$ s^{-1}
0·016	0·08	6·48	2·35
0·008	0·08	6·07	2·17
0·004	0·08	6·03	2·15
0·002	0·08	6·60	2·37
0·004	0·16	9·47	2·38
0·004	0·04	4·33	2·18
0·004	0·02	2·92	2·06

$$-d[Fe(CN)_6{}^{3-}]/dt = 0{\cdot}0221[Fe(CN)_6{}^{3-}][HNO_2]^{\frac{1}{2}} \text{ mol dm}^{-3}\text{ s}^{-1} \quad (6)$$

k_2 gave an Arrhenius activation energy of 64·2 kJ mol^{-1}. Plots of [Intermediate] against time showed a smooth increase in [Intermediate] from zero time, with no sign of any induction period. A few runs were carried out in which both the formation of the intermediate and the disappearance of $[Fe(CN)_6]^{3-}$ ion were followed. A typical example is shown in Table 2, and is discussed at the end of this paper.

TABLE 2

Comparison of the loss of hexacyanoferrate(III) with formation of the intermediate at 25 °C

t/min	0·5	1·0	1·5	2·0	3·0
$-10^3\Delta[Fe(CN_6{}^{3-}]$/ mol dm^{-3}	1·17	1·92	2·50	3·05	3·77
10^3[Intermediate] mol dm^{-3}	0·83	1·55	2·20	2·73	3·70
t/min	4·0	6·0	8·0	10·0	
$-10^3\Delta[Fe(CN_6{}^{3-}]$/	4·44	5·57	6·42	6·90	
10^3[Intermediate]/ mol dm^{-3}	4·50	5·58	6·25	6·72	

$[Fe(CN)_6{}^{3-}]_0$ = 0·008, $[HNO_2]_0$ = 0·04, and $[HNO_3]$ = 6 mol dm^{-3}.

Nitrite analysis. Runs were carried out with a five- to ten-fold excess of $[Fe(CN)_6]^{3-}$ ion over HNO_2. Individual runs gave good 'half-order' plots of $([HNO_2]_0^{\frac{1}{2}} - [HNO_2]^{\frac{1}{2}})$ against time over two to three half-lives, and $k_{\frac{1}{2}}$ values were constant over a 20-fold variation in initial $[HNO_2]$. The overall rate law was $-d[HNO_2]/dt = k_{\frac{1}{2}}[HNO_2]^{\frac{1}{2}} = 0{\cdot}0101$ $[Fe(CN)_6{}^{3-}][HNO_2]^{\frac{1}{2}}$ mol dm^{-3} s^{-1} in 6 mol dm^{-3} nitric acid at 25 °C. A few typical results are shown in Table 3, including runs with varying nitric acid concentration. Initial concentrations of HNO_2 obtained by extrapolation of the 'half-order' plots to zero time were slightly lower (on average 6%) than the expected values, and this was attributed to the instability of HNO_2.

TABLE 3

Rate constants for the disappearance of nitrous acid, in nitric acid at 25 °C

$[HNO_3]$ / mol dm^{-3}	$[Fe(CN)_6{}^{3-}]$ / mol dm^{-3}	$[HNO_2]$ / mol dm^{-3}	$10^5k_{\frac{1}{2}}$ / mol$^{\frac{1}{2}}$ dm$^{-3/2}$ s^{-1}	10^3k_3 / mol$^{-\frac{1}{2}}$ dm$^{3/2}$ s^{-1}
6	0·01	0·002	9·4	9·4
6	0·01	0·0005	9·4	9·4
6	0·01	0·0001	8·2	8·2
6	0·005	0·0001	4·7	9·4
6	0·02	0·0001	20·6	10·3
7	0·01	0·001	15·0	15·0
4·5	0·01	0·0001	3·9	3·9
3·5	0·01	0·001	2·2	2·2

$k_3 = k_{\frac{1}{2}}/[Fe(CN)_6{}^{3-}]$.

Intermediate analysis. A limited number of runs were followed by the appearance of the intermediate species, and the rate law was found by the method of initial rates. If the initial rate of appearance of co-ordinated nitrosyl in the intermediate is v_0, then $v_0 = 0{\cdot}017$ $[Fe(CN)_6{}^{3-}][HNO_2]^{\frac{1}{2}}$ mol dm^{-3} s^{-1} in 6 mol dm^{-3} nitric acid at 25 °C. This rate is markedly lower than the value from $[Fe(CN)_6]^{3-}$ analysis. We have evidence that $[Fe(CN)_6]^{3-}$ ion interferes with the analysis for the intermediate, and we think that $[Fe(CN)_6]^{3-}$ analysis gives a more reliable value.

Kinetics of stage (*iii*). The only method that was found for studying this stage was to follow spectrophotometrically the disappearance of the characteristic peak at 382 nm. The absorbance A decreased to zero, and plots of log A against time were linear over two to three half-lives. The rate constant, k_4, was virtually independent of the concentration of the intermediate, and nitric and nitrous acids. Measurements of the effect of temperature gave an Arrhenius activation energy of 63 kJ mol^{-1}.

TABLE 4

Kinetics of decay of the intermediate in nitric acid at 25 °C

10^3[Intermediate] / mol dm^{-3}	$[HNO_3]$ / mol dm^{-3}	$[HNO_2]$ / mol dm^{-3}	10^4k_4 / s^{-1}
7·3	5·5		2·90
3·6	5·5		2·72
1·8	5·5		2·72
3·6	5·5		2·72
3·6	4·7		2·44
3·6	4·0		2·40
3·6	2·7		2·35
3·6	1·4		2·32
7·3	5·5	0·118	2·75
7·3	5·5	0·130	2·70
3·6	2·7	0·078	2·34

Experiments in perchloric and sulphuric acids. The change in the rate of reaction with $[HNO_3]$ may be a combination of effects due to changes in acidity and in nitrate concentration. To separate these we examined the reaction in perchloric and sulphuric acids with low concentrations of nitric acid. The same general features appeared. There was a rapid initial decrease in the intensity of the $[Fe(CN)_6]^{3-}$ peak, followed by a much slower change. The initial drop in absorbance was much more rapid than in 6 mol dm^{-3} nitric acid and was complete in a few seconds. Work described in a previous paper has shown that this is due to the establishment of equilibrium (2). Runs with a large excess of $[Fe(CN)_6]^{3-}$ over HNO_2 were followed by the decrease in $[HNO_2]$ and gave good ' half-order ' plots as before, but values of $[HNO_2]_0$ obtained by extrapolation to zero time were substantially lower than expected from the concentration added initially.

For stage (*ii*) we studied the reaction in sulphuric acid, with a constant excess of $[Fe(CN)_6]^{3-}$ ion and HNO_3 in any one run. Good half-order plots were obtained over two half-lives, and $k_{\frac{1}{2}}$ varied linearly with $[Fe(CN)_6{}^{3-}]$, *i.e.* the same form of rate law as that in 6 mol dm^{-3} nitric acid. For runs with constant $[HNO_3]$, plots of log $k_{\frac{1}{2}}$ against H_- gave a gradient of $+0{\cdot}52 \pm 0{\cdot}11$ over the range 2·9—4·5 mol dm^{-3} sulphuric acid. Another set of runs in 3·4 mol dm^{-3} sulphuric acid, and with various nitric acid concentrations, gave a linear plot of log $k_{\frac{1}{2}}$ against log $[HNO_3]$ with a gradient of 0·795. Here $[HNO_3]$ is the stoicheiometric concentration of nitric acid (which will, of course, be partly ionised). The results are in Table 5. We chose 3·4 mol dm^{-3} sulphuric acid for comparison with 6 mol dm^{-3} nitric acid because the two media [6] have the same H_0 value. It would have been preferable to use solutions with the same H_- value, but data were not available [7] for nitric acid. If we express the rates of reaction in 6 mol dm^{-3} nitric acid and 3·4 mol dm^{-3} sulphuric acid–0·1 mol dm^{-3} nitric acid in the form $-d[HNO_2]/dt = k[Fe(CN)_6{}^{3-}][HNO_2]^{\frac{1}{2}}[HNO_3]^{\frac{1}{2}}$, then values of k are 0·0041 and 0·0165 mol^{-1} dm^3 s^{-1} respectively. Considering the difference in the two media, our assumption that they both have the same acidity and the fact that we have had to use the stoicheiometric nitric acid concentration (tacitly assuming the degree of dissociation is the same in each case), we are satisfied that the two sets of results are consistent.

TABLE 5

Dependence of $k_{\frac{1}{2}}$ values on acidity and nitric acid concentration

$[H_2SO_4]$ [a] / mol dm^{-3}	$10^5k_{\frac{1}{2}}$ / mol$^{\frac{1}{2}}$ dm$^{-3/2}$ s^{-1}	$[HNO_3]$ [b] / mol dm^{-3}	$10^5k_{\frac{1}{2}}$ / mol$^{\frac{1}{2}}$ dm$^{-3/2}$ s^{-1}
2·9	1·58	1·0	7·00
3·4	2·75	0·8	5·20
4·0	4·83	0·4	3·03
4·5	6·66	0·2	1·93
4·5	6·66	0·1	1·04

[a] $[Fe(CN)_6{}^{3-}] = 0{\cdot}024$, $[HNO_2] = 0{\cdot}001$, and $[HNO_3] = 0{\cdot}2$ mol dm^{-3}. [b] $[Fe(CN)_6{}^{3-}] = 0{\cdot}002$, $[HNO_2] = 0{\cdot}001$, and $[H_2SO_4] = 3{\cdot}4$ mol dm^{-3}.

DISCUSSION

The kinetics of stage (*ii*) are of the form $-d[Fe(CN)_6{}^{3-}]/dt = -2d[HNO_2]/dt = k[Fe(CN)_6{}^{3-}][HNO_2]^{\frac{1}{2}}$. The same form of rate law has also been observed for formation of the intermediate. The half-order dependence on nitrous acid is undoubtedly real, and is observed over a 1 000-fold change in $[HNO_2]$; it cannot be explained as an average value due to parallel zero- and first-order reactions, or to a single mechanism with a transition from zero- to first-order kinetics. The dependence of k on acidity and nitrate concentration is less certain. We used H_- as the most suitable measure of acidity,[7] because with $[Fe(CN)_6]^{3-}$ as a reactant it is probable that the transition state bears an overall negative charge. There are little quantitative data on this function. Many investigations have shown that different acidity functions are required to describe the protonation of different classes of neutral bases and this is probably true for negatively charged bases. The gradient of $-0{\cdot}52$ for plots of log k against H_- is certainly consistent with an ideal order of $\frac{1}{2}$, but could also be consistent with other values. The order of 0·795 in nitrate is probably too high because the addition of sizeable concentrations of HNO_3 to 3·4 mol dm^{-3} sulphuric acid will increase the acidity of the medium. We have attempted to correct for this by measuring the effect of added HNO_3 on the value of H_0 for H_2SO_4 solutions. By assuming the change in H_- is the same as that in H_0 we can correct for the increase in rate due to increase in acidity. When this is allowed for, the order in nitrate is 0·6.

The fact that the rate law is half order in HNO_2 and close to half order in nitrate strongly suggests that nitrogen dioxide is involved as a reactant. The mechanism by which this is formed in aqueous solutions of nitric acid is well known, and we may write the mechanism in equations (3)—(5). In dilute solution this would give rise to the rate law $v = k_5K_1{}^{\frac{1}{2}}K_2{}^{\frac{1}{2}}[Fe(CN)_6{}^{3-}][H^+]^{\frac{1}{2}}[HNO_2]^{\frac{1}{2}}[NO_3{}^-]^{\frac{1}{2}}$. In 6 mol dm^{-3} nitric acid the corresponding rate law is $v = k_5K_1{}^{\frac{1}{2}}K_2{}^{\frac{1}{2}}\beta[Fe(CN)_6{}^{3-}]h_-{}^{\frac{1}{2}}[HNO_2]^{\frac{1}{2}}[NO_3{}^-]^{\frac{1}{2}}$, where $\beta = K_3{}^{\frac{1}{2}}\gamma^{\frac{1}{2}}{}_1\gamma_2{}^{\frac{1}{2}}\gamma_3/[(K_3 + h_-)^{\frac{1}{2}}a_4{}^{\frac{1}{2}}\gamma_{\ddagger}]$. In this expression γ_1, γ_2, γ_3, and $\gamma_{\ddagger}$ are activity coefficients of molecular HNO_2, HNO_3,[6] $[Fe(CN)_6]^{3-}$, and the transition state respectively, and a_4 is the activity of water; K_3 is the thermodynamic dissociation constant and h_- is an acidity function appropriate to the ionisation of nitric acid. The values of γ_2 and $(K_3 + h_-)$ will increase, and the activity of water will decrease, with increasing mineral acid concentration. However, γ_1 and the ratio $\gamma_3 : \gamma_{\ddagger}$ are not likely to vary much. Thus there will be some cancellation in changes in the terms composing β, and our interpretation of the rate law, which requires only a small variation in β from 2·9 to 4·5 mol dm^{-3} sulphuric acid, is reasonable. In view of the uncertainty about the variation of these activity coefficients and the fact that we are assuming Boyd's acidity function is appropriate for protonation of the nitrate ion, we attach no significance to the difference between the observed order of 0·59 and the ideal order of 0·5 in h_-.

On the basis of this mechanism we may attempt to account for the variation in rate with $[HNO_3]$. Over the range 3·5—7·0 mol dm^{-3} stoicheiometric HNO_3, a plot of log k against log $[HNO_3]$ has gradient 3·0. Using known values [8] of the degree of dissociation and activity coefficients for aqueous nitric acid, and assuming the constancy of $\gamma_3\gamma_1/\gamma_{\ddagger}$, we expect a gradient of 2·2. Alternatively

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[6] F. A. Long and M. A. Paul, *Chem. Rev.*, 1957, **57**, 1.

[7] R. H. Boyd, *J. Amer. Chem. Soc.*, 1961, **83**, 4288.

[8] W. Davis and H. J. de Bruin, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1069.

using Boyd's data for H_- and assuming that the difference between H_0 and H_- is constant over the range of $[HNO_3]$ considered, we calculate a gradient of 3·46. Both these methods are very approximate, but they bracket the observed dependence of rate on stoicheiometric $[HNO_3]$, and we are reasonably satisfied with our explanation.

Our mechanism requires equilibria (3) and (4) to be established rapidly. The rates of the forward and reverse reactions are known in both cases, and this condition is met. We have tacitly assumed that nitrogen dioxide and dinitrogen tetra-oxide are only a small proportion of the total HNO_2. The spectrophotometric data of Longstaff and Singer[9] provide direct evidence for this. The mechanism is also consistent with our measured stoicheiometry. One mole of NO_2 is produced from half a mole of HNO_2 and half a mole of HNO_3, and clearly our mechanism requires $\Delta[Fe(CN)_6{}^{3-}]/\Delta[HNO_2] = 2$ as is found experimentally. This also accounts for the fact that one mole of HNO_2 produces two moles of co-ordinated nitrosyl in the intermediate; each nitrosyl group is derived half from nitrite and half from nitrate. Anticipating the discussion in the following paper, we believe that the NO_2 oxidises a cyanide ligand to cyanate. Some of the cyanate then undergoes hydrolysis to yield ammonia and carbon dioxide, and some of the cyanate and hydrogen cyanide is converted to cyanogen.

An alternative explanation of the half-order dependence on $[HNO_2]$ is a reaction involving a small equilibrium concentration of $[Fe(CN)_6]^{4-}$ ion. Equilibrium (2) leads to the expression $[Fe(CN)_6(H)_2{}^{2-}] = K[Fe(CN)_6{}^{3-}]$-$[HNO_2]^{\frac{1}{2}}[H^+]/[HNO_3]^{\frac{1}{2}}$. Rate-determining hydrolysis of $[Fe(CN)_6]^{4-}$ ion would be consistent with the half-order dependence on $[HNO_2]$, and would be similar to the mechanism reported by Seel[1] for reaction in hydrogen carbonate buffers [equation (7)]. Such a mechanism is

$$[Fe(CN)_6(H)_2]^{2-} \xrightarrow[\text{slow}]{H^+,H_2O}$$

$$HCN + [Fe(CN)_5H_2O]^{3-} \xrightarrow[\text{fast}]{H^+,HNO_2} [Fe(CN)_5NO]^{2-} \quad (7)$$

also attractive because we have shown that a small amount of $[Fe(CN)_6]^{4-}$ ion is formed in equilibrium with $[Fe(CN)_6]^{3-}$ and HNO_2 and HNO_3. However such a mechanism would give a rate inhibited by nitrate, whereas our reaction is catalysed by nitrate. Furthermore this would lead to a stoicheiometry $\Delta[Fe(CN)_6{}^{3-}]/\Delta[HNO_2] = 0{\cdot}66$, a wrong yield of hydrogen cyanide, and would not account for the ammonia formed. It is also clear, as discussed in the following paper, that our product in stage (*ii*) is not $[Fe(CN)_5NO]^{2-}$. To account for our results in terms of $[Fe(CN)_6]^{4-}$ ion, it is necessary to postulate the reaction (8). This seems very improbable. In

$$HNO_3 + [Fe(CN)_6(H)_2]^{2-} \longrightarrow \text{Intermediate} \quad (8)$$

media as aqueous as 6 mol dm^{-3} nitric acid all reactions of HNO_3 seem to involve HNO_2 catalysis. Emschwiller[10] studied the aquation of $[Fe(CN)_6]^{4-}$ ion and found the rate to increase with decreasing pH, reaching a maximum at pH 4. His rates of aquation are some 10^5 times slower than those for disappearance of $[Fe(CN)_6]^{3-}$ ion obtained in this work. This is not particularly strong evidence, as our solutions were so much more acidic than his. More direct evidence is that a solution of 10^{-3} mol dm^{-3} hexacyanoferrate(II) in 5·1 mol dm^{-3} sulphuric acid at 25 °C showed no increase in absorbance at 400 nm over a period of 1 h. At this wavelength, absorption coefficients of the ions $[Fe(CN)_5H_2O]^{3-}$ and $[Fe(CN)_6]^{4-}$ are reported to be 1 080 and 4 dm^3 mol^{-1} cm^{-1} respectively,[11] so any aquation should be readily detectable. Furthermore a solution of $[Fe(CN)_6]^{4-}$ ion in 6 mol dm^{-3} nitric acid, containing sulphamic acid to remove the last traces of nitrite, showed no sign of formation of the intermediate. If, instead of a rate-determining aquation, one postulates direct nitrosation of $[Fe(CN)_6]^{4-}$ ion, then the mechanism no longer predicts the order of one half in $[HNO_2]$, as this has already been accounted for in the initial redox equilibrium. We think that reaction through $[Fe(CN)_6]^{4-}$ ion can be excluded as a mechanism for stage (*ii*).

One feature of the kinetics that is not understood is the size of the initial decrease in the $[Fe(CN)_6]^{3-}$ peak at 420 nm during the first 1—2 min of reaction [stage (*i*)]. Equilibrium constants for (1) obtained from e.m.f. measurements predict only a small conversion of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ ion, a few per cent, rather than the 20—25% observed. Furthermore equilibrium (2) is established very much more rapidly in sulphuric and perchloric acids [where it can be studied without interference from stage (*ii*)] than stage (*i*) occurs in 6 mol dm^{-3} nitric acid. However, the kinetic plots for the disappearance of $[Fe(CN)_6]^{3-}$ ion, of HNO_2, and the appearance of the intermediate show no abnormal behaviour in this region. Inspection of the results in Table 2 shows that, although there is good agreement between the disappearance of $[Fe(CN)_6]^{3-}$ ion and the appearance of the intermediate over most of the run, there is a difference in the first 2 min, amounting to *ca.* 4% of the initial $[Fe(CN)_6{}^{3-}]$. The analytical method for determining the intermediate is based on a calibration curve from a $[Fe(CN)_5NO]^{2-}$ standard, and we know that $[Fe(CN)_6]^{3-}$ ion interferes with the method. The 4% difference is much smaller than the size of the initial decrease in the 420 nm peak. Attempts to identify other species present in the initial stages, by precipitation with silver(I) nitrate, were unsuccessful and we cannot explain satisfactorily what is happening in stage (*i*) of the reaction.

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[9] J. V. L. Longstaff and K. Singer, *J. Chem. Soc.*, 1954, 2610.

[10] G. Emschwiller, *Compt. rend.*, 1953, **236**, 72; 1955, **241**, 44.

[11] B. Jaselskis and J. C. Edwards, *Analyt. Chem.*, 1960, **23**, 381; J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, 1966, **5**, 573.