Note

The Mechanism of Oxidation of Hexacyanoferrate(II) by Nitrous Acid

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The kinetics of oxidation of $[Fe(CN)_6]^{3-}$ by nitrous acid at 25 °C have been studied. Reaction is acid catalysed at low acidities, $[H^+] = 0.01$ mol dm^{-3}, but the rate is independent of acidity at $[H^+] = 0.5$ mol dm^{-3}. Reaction is encounter controlled and occurs between $[HFe(CN)_6]^{3-}$ and $[NO]^+$.

THE redox equilibrium (1) has been studied by spectrophotometric and e.m.f. methods and it is known[1] that at low acidities the formation of ferricyanide [hexacyanoferrate(III)] is favoured, whereas at higher acidities ferrocyanide [hexacyanoferrate(II)] is favoured.

$$H_2O + HNO_2 + 2[Fe(CN)_6]^{3-} \rightleftharpoons HNO_3 + 2[Fe(CN)_6]^{4-} + 2H^+ \quad (1)$$

The main factor involved in this shift of equilibrium is the basicity of ferrocyanide, which can accept up to four protons. The dissociation constants of $[HFe(CN)_6]^{3-}$ and $[H_2Fe(CN)_6]^{2-}$ are known[2] and these species are formed in dilute (0.1 mol dm^{-3}) mineral acid. The formation constants of the tri- and tetra-protonated species are not known. We have been concerned with the reactions occurring in a solution containing ferricyanide and ferrocyanide in a medium of nitric acid + nitrous acid,[3] and the object of the present work was to examine the mechanism of the reaction between ferrocyanide and nitrous acid at relatively low acidities, free from complications due to nitric acid. Under these conditions reaction (2) is observed.

$$HNO_2 + H^+ + [Fe(CN)_6]^{4-} \longrightarrow NO + H_2O + [Fe(CN)_6]^{3-} \quad (2)$$

EXPERIMENTAL

All materials were AnalaR chemicals, used without further purification. Because aqueous solutions of ferrocyanide may undergo photochemical, hydrolytic, or oxidation reactions in acidic media, all runs were carried out with freshly prepared solutions. Experiments carried out with deoxygenated solutions showed that under our conditions dissolved dioxygen had no effect on the rate of reaction. The kinetics were followed by stopped-flow spectrophotometry, using a Canterbury SF-3A instrument, measurements of the absorbance A being made at 418 nm. At this wavelength ferricyanide has a peak with a high absorption coefficient, $\varepsilon = 1\ 050$ dm^3 mol^{-1} cm^{-1}, while the absorption of ferrocyanide is negligible. All experiments were carried out in perchloric acid solution at 25 °C (except for the activation-energy measurements). Where necessary, solutions were maintained at constant ionic strength by the addition of sodium perchlorate.

RESULTS AND DISCUSSION

All runs were carried out with a large excess of nitrous acid over ferrocyanide, and gave linear plots of $\ln(A_\infty - A)$ *vs.* time over several half-lives. Typical ferrocyanide concentrations were around 5×10^{-5} mol dm^{-3}. The first-order rate constant k_1 was independent of the initial concentration of ferrocyanide, confirming the first-order rate law. When the concentration of excess of nitrous acid was varied by a factor of four a plot of log k_1 against log[HNO_2] gave a slope of 0.91, thus showing the rate of reaction to be first order with respect to nitrous acid concentration. Some of our results are shown in the Table. If we take [ferro] to be the total concentration of ferrocyanide conjugate acid–base species, then the results fit equation (3).

Rate constants for the oxidation of ferrocyanide by nitrous acid in 0.1 mol dm^{-3} perchloric acid at 25 °C ($I = 0.1$ mol dm^{-3})

10^5[ferro]/mol dm^{-3}	5	5	5	5	5 *	10	2.5
$10^4[HNO_2]$/mol dm^{-3}	5	5	2.5	10	5	5	5
k_1/s^{-1}	0.726	0.711	0.351	1.23	0.734	0.672	0.683

* Deoxygenated solution.

$$-d[\text{ferro}]/dt = k_1[\text{ferro}] = k_2[\text{ferro}][HNO_2] \quad (3)$$

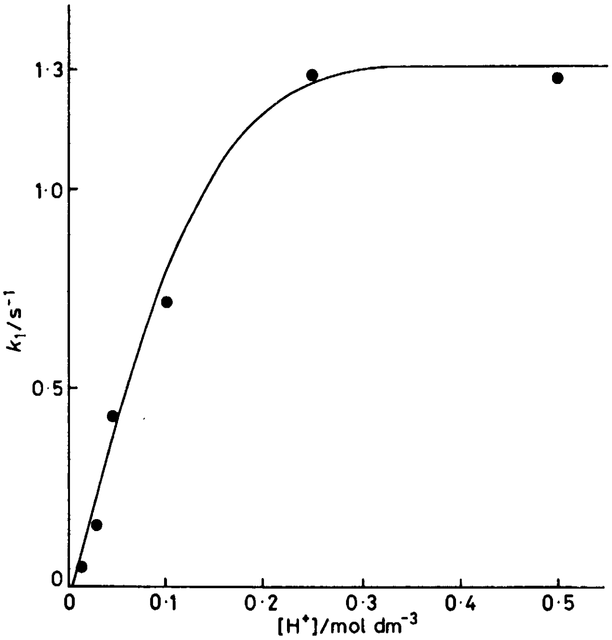
A plot of the variation of k_1 with acidity for reaction with 5×10^{-4} mol dm^{-3} nitrous acid at $I = 1$ mol dm^{-3} is shown in the Figure; at low acidities the rate law takes the form of equation (4) while at high acidities (5) holds. Equation (4) is the form of rate law found for

$$v = k_3[H^+][HNO_2][\text{ferro}] \quad (4)$$

$$v = k_4[HNO_2][\text{ferro}] \quad (5)$$

reaction between the nitrosonium ion and a wide range of nucleophiles that are only weakly basic; equation

(5) is the form observed for reaction of the nitrosonium ion with basic nucleophiles.[4] From the known ionisation constants of $[HFe(CN)_6]^{3-}$ and $[H_2Fe(CN)_6]^{3-}$ (pK_a at $I = 0$: 4.17 and 2.22 respectively) it can be calculated that at the lowest acidity studied, $[H^+] =$ 0.01 mol dm^{-3}, the bulk component of ferrocyanide is $[Fe(CN)_6]^{3-}$, while at the highest acidity ($[H^+] = 0.5$ mol dm^{-3}) it is $[H_2Fe(CN)_6]^{2-}$. Thus a simple explanation of the kinetics is a rate-determining reaction between $[NO]^+$ and $[HFe(CN)_6]^{3-}$ [equations (6) and (7)]. At low



Variation of k_1 with perchloric acid for the oxidation of ferrocyanide by excess of nitrous acid (5×10^{-4} mol dm^{-3}) at $I = 1$ mol dm^{-3} and 25 °C

$$H^+ + HNO_2 \rightleftharpoons [NO]^+ + H_2O \qquad \text{fast (6)}$$

$$[NO]^+ + [HFe(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + H^+ + NO \qquad \text{slow (7)}$$

acidities where [ferro] $= [HFe(CN)_6{}^{3-}]$ this would lead to equation (4), while at higher acidities where the bulk component of ferrocyanide is the doubly protonated species, $[H_2Fe(CN)_6{}^{2-}] = [HFe(CN)_6{}^{3-}][H^+]K_a{}^{-1} =$ [ferro], the rate would be independent of acidity as in (5). In the above equation K_a is the dissociation constant of $[H_2Fe(CN)_6]^{2-}$. The mechanism of (7) may be a straight outer-sphere electron transfer, but it could also involve the formation of a nitrosylferrocyanide, $[(NC)_5H\text{-}FeCN\text{-}NO]^{2-}$, which might break down by homolytic fission of the N-N bond. As reaction seems to be encounter controlled (see below) the kinetics do not distinguish between these possibilities. This mechanism is basically identical to that found[5] for the oxidation of $[Fe(phen)_2(CN)_2]$ and $[Fe(bipy)_2(CN)_2]$ by nitrous acid (phen = 1,10-phenanthroline; bipy = 2,2'-bipyridyl).

Many reactions of anions with the nitrosonium ion are encounter controlled,[4] and for a singly charged anion the value corresponding to k_3 in (4) is *ca.* 14 000 dm^6 mol^{-2} s^{-1} at 25 °C. A formula for calculating the effect of coulombic charge on the encounter rate is known,[6] and for a triply charged ion such as $[HFe(CN)_6]^{3-}$ k_3 would be expected to be *ca.* 32 000 dm^6 mol^{-2} s^{-1} at 25 °C. The rate constant calculated from the first-order part of our curve is *ca.* 16 600 dm^6 mol^{-2} s^{-1}. This appears to be the first experimental value for the rate of reaction of a triply charged anion with $[NO]^+$. A further point in favour of this interpretation is that we find the activation energy to be 53.5 kJ mol^{-1} (measured over the range 0—25 °C), which compares very well with the activation energy for other encounter reactions of the nitrosonium ion of *ca.* 54 kJ mol^{-1}. From the variation of k_1 with acidity one can obtain a value for the pK_a of $[HFe(CN)_6]^{3-}$. The points for 0.1 and 0.05 mol dm^{-3} perchloric acid from the Figure give pK_a values (corrected from $I = 1$ to 0 mol dm^{-3} by the Davies equation) of 1.94 and 1.85 respectively. These compare satisfactorily with the literature value of 2.22, if one considers the approximations made.

The main reservation that we have about this mechanism is that it ascribes all the redox reactivity to one ferrocyanide species, $[HFe(CN)_6]^{3-}$, and it might reasonably be asked why $[H_2Fe(CN)_6]^{2-}$ is not active too. In survey experiments we have found no sign of any increase in rate up to 2 mol dm^{-3} perchloric acid, so there is no sign of a term of the form $v = k[H^+][HNO_2][H_2Fe(CN)_6{}^{2-}]$ in the rate law. One possible explanation is that by the Frank-Condon principle a rapid electron transfer would result in the formation of a doubly protonated ferricyanide as a product, and this would be expected to be an unstable species as ferricyanide shows no sign of any basic behaviour in the acidity range we are studying. Such a pathway might have a high activation energy. There may, however, be small contributions to the reaction rate by redox pathways involving $[Fe(CN)_6]^{4-}$ as a reductant, or possibly involving ion pairs such as $[Fe(CN)_6Na]^{3-}$. As we are working in a region of ionic strength well outside the range of the extended Debye-Hückel treatment, and we are dealing with ions with large charges, it seems unduly speculative to try to allow for these in a quantitative treatment of the rate data.

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