Redox Equilibrium between Ferricyanide, Ferrocyanide, and Nitric and Nitrous Acids

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The redox equilibrium between nitrous acid and ferricyanide and nitric acid and ferrocyanide has been investigated by spectrophotometric and e.m.f. methods. The results agree closely, and show the equilibrium to be a very sensitive function of acidity.

DURING the course of a study of the kinetics and mechanism of the reaction between potassium ferricyanide [hexacyanoferrate(III)] and nitric and nitrous acids[1] it became clear that the redox equilibrium (1) was rapidly established. However the rate of the next stage of the reaction, attack by nitrogen dioxide on ferricyanide to produce an intermediate species similar to nitroprusside, was sufficiently great to overlap with establishment of (1). In order to study the initial equilibrium free from this complication we have used perchloric and sulphuric acids as solvents, with low concentrations of nitric and nitrous acid. Under these conditions the concentration of nitrogen dioxide is low, and there is negligible interference from later reactions. We have studied the equilibrium by spectrophotometry and by e.m.f. measurements of the ferricyanide–ferrocyanide and nitric acid–nitrous acid couples. There are a number of isolated measurements of these potentials in the literature[2] but nothing sufficiently systematic for our needs.

$$2H^+ + 2Fe(CN)_6{}^{3-} + HNO_2 + H_2O \rightleftharpoons 2Fe(CN)_6H_2{}^{2-} + HNO_3 \quad (1)$$

EXPERIMENTAL

AnalaR chemicals were used without further purification. Solutions of potassium ferricyanide and potassium ferrocyanide were freshly prepared before use, stored in blackened bottles, and kept out of light as much as possible.

Spectrophotometric measurements were made with Unicam SP 500, Unicam SP 700, and Carey 16 instruments, with thermostatted cell holders or cell compartments, with solutions brought to temperature equilibrium before mixing. Experiments in which the temperature was varied from 16 to 35 °C showed no detectable variation in the equilibrium constant, so this parameter is not very important. In most experiments a solution of ferricyanide was added to perchloric acid + nitric acid + nitrous acid, and the decrease in absorbance of the ferricyanide peak at 420 nm (ε 1000 l mol^{-1} cm^{-1}) was measured (at this wavelength the other species have negligible absorption). At low wavelengths (260 nm) ferrocyanide absorbs more strongly than ferricyanide, and we confirmed that here the absorbance *increased*, in contrast to the decrease at 420 nm. Solutions reached an equilibrium absorbance within 30 s of mixing.

The measurements of e.m.f. were made by standard methods with a Solartron digital voltmeter. A saturated calomel electrode was used as a reference with a saturated solution of potassium nitrate as a salt bridge. Equilibrium was attained very rapidly with the ferricyanide–ferrocyanide system, but with the nitric acid–nitrous acid system it was necessary to take readings during a period of minutes before they became steady.

RESULTS AND DISCUSSION

In view of the fact that mixtures of nitric and nitrous acids are commonly thought of as an oxidising system, we begin with direct chemical evidence that they reduce ferricyanide to ferrocyanide. Samples of the reaction mixture, 6M-nitric acid, 0·04M-nitrous acid, and 0·008M-ferricyanide at 25 °C were quenched shortly after reaction started by the addition of 2·5M-urea solution. This destroyed the nitrous acid. Silver nitrate solution was added, and the resulting precipitate washed, dried, and examined by i.r. spectroscopy in Nujol mull. The spectra showed the presence of a sharp peak at 2170 cm^{-1} characteristic of ferricyanide, but also a small, broad peak at 2040 due to ferrocyanide. Experiments in which the precipitation by silver nitrate was carried out without prior quenching with urea gave much more

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[1] K. M. Davies and G. Stedman, *Chem. Comm.*, 1968, 118.

[2] H. H. Willard and G. D. Manalo, *Analyt. Chem.*, 1947, **19**, 462; R. G. Monk and H. J. T. Ellingham, *J. Chem. Soc.*, 1935, 125.

intense bands at 2040 cm^{-1}. A separate experiment in 7M-perchloric acid, 0·01M-nitrous acid, and 0·001M-ferricyanide rapidly yielded a colourless solution in which there was no visible trace of the ferricyanide peak at 420 nm. Addition of a known excess of silver nitrate, filtration, and back titration of the excess of silver showed that 4·3 mol of silver were removed per mol of original ferricyanide. The white precipitate showed the characteristic band at 2040 cm^{-1}, with no sign of the peak at 2170 cm^{-1}. Further experiments in 4·8 and 6·1M-perchloric acid, in which nitrous acid and ferricyanide were mixed, allowed to reach equilibrium, and the final solution analysed for both components gave ratios $\Delta[Fe(CN)_6{}^{3-}]/\Delta[HNO_2]$ of 2·0 and 1·8 respectively, consistent with equation (1).

Spectrophotometric measurements of equilibrium (1) were made with solutions in which the nitric and nitrous acids were in constant excess, and it was only the ratio of ferricyanide to ferrocyanide that varied. This ratio was taken to be $(A_0 - A)/A$, where A was the absorbance at 420 nm, and A_0 the value corresponding to the initial amount of ferricyanide present. An equilibrium constant $K = [\text{ferro}][\text{nitrate}]^{\frac{1}{2}}/[\text{ferri}][\text{nitrite}]^{\frac{1}{2}}$ was calculated, where [ferri], [ferro], [nitrate], and [nitrite] represent the total stoicheiometric concentrations of these species. Experiments in which ferrocyanide was added initially instead of ferricyanide gave identical results, showing that the equilibrium can be approached from either side. A typical set of results is shown in the Table. Similar results were obtained at other perchloric acid concentrations. Some of these measurements are shown in the Figure; others have been omitted for clarity.

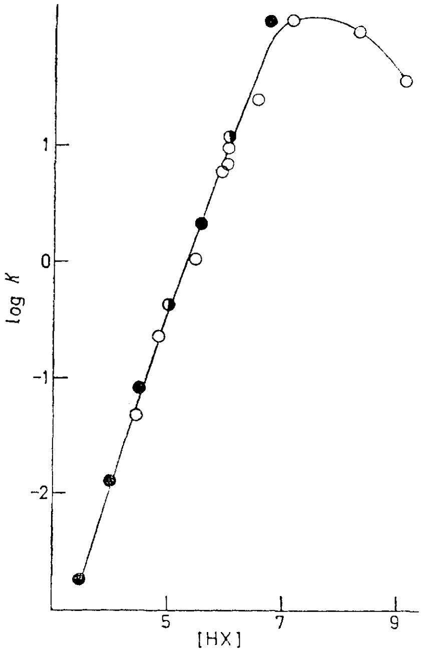
Spectrophotometric measurements of equilibrium (1) in 5·5M-perchloric acid

$10^4[\text{ferri}]_0$	8	8	8	8 [a]	8	5
$10^2[\text{nitrate}]_0$	10	4	1	10	4	4
$10^2[\text{nitrate}]_0$	1	1	1	1	2	1
K	2·4	2·4	1·9	2·4	1·8	2·0

[a] Ferrocyanide was used in place of ferricyanide.

It seemed desirable to obtain confirmatory evidence by another technique, and hence the e.m.f. of cells involving the ferricyanide–ferrocyanide and the nitric acid–nitrous acid couples were measured. Plots of E against log [ferri]/[ferro] were linear, with slopes in agreement with the theoretical value of $2{\cdot}303RT/F$, and from the intercept E_0 values were obtained. Results for the nitric acid–nitrous acid couple were obtained in a similar way. Values of K calculated from the E_0 data are shown in the Figure. They agree well with the spectrophotometric results. However the e.m.f. measurements can be extended over a much wider range of mineral acid concentration than the spectrophotometric technique, and in particular can readily be applied to solutions of low acidity, where conversion of ferricyanide into ferrocyanide is too small to be measured accurately. We have also carried out spectrophotometric determinations of K in 4·5, 5·0, 5·5, and 6·0M-sulphuric acids, and these results fall on the same graph, within experimental error. In view of the fact that solutions of sulphuric and perchloric acids of a given molarity have the same value of H_0 to within 0·15 unit from 1 to 6M, this is not too surprising.

In addition to the above results, we also needed to obtain a value of K for 6M-nitric acid, the medium used in our other mechanistic studies. Monk and Ellingham [2] have already reported E_0 values for the nitric acid–nitrous acid couple, so we only needed the corresponding value for the ferricyanide–ferrocyanide system. A variety of qualitative observations and also a detailed kinetic study showed that nitrous acid was an essential catalyst for both the forward and back reactions of (1). When a reagent such as urea or sulphamic acid is added to nitric acid, all traces of nitrous acid are destroyed, and it is possible to add ferricyanide and ferrocyanide and measure the redox couple without interference from equilibrium (1). Such measurements need to be made within a few minutes of mixing, because during a period of hours another reaction occurs, involving the formation of a blue precipitate. When these measurements were combined with those of Monk and Ellingham it was possible to calculate that $K = 0{\cdot}12$ for our reaction solution in 6M-nitric acid.



Variation of log K with mineral acid concentration/M; ○, spectrophotometry ($HClO_4$); ●, e.m.f. ($HClO_4$); and ◑, spectrophotometry (H_2SO_4)

The most striking feature of these results is the extreme sensitivity of K to the mineral acid concentration, and the rather sudden change in slope above 7M-perchloric acid. An increase in K with acidity is implicit in equation (1), but there are likely to be large effects owing to changes in activity coefficients, and also to acid–base equilibria. It is difficult to account quantitatively for the former, but we can discuss the latter. Nitric acid is a moderately strong acid,[3] $K_a = 15$. If the protonation of the nitrate ion follows Boyd's H_- acidity function,[4] then it should be at least 90% in the protonated form above 3·9M-perchloric acid and this equilibrium cannot have much effect upon K. Nitrous acid in perchloric acid forms the nitrosonium ion, and this equilibrium follows [5] H_R with a pK of −8·11. Thus nitrite should exist as more than 90% molecular HNO_2 below 6·45M-perchloric acid, but will be only 50% in this form by 7·15M. Clearly this change may be partly responsible for the change in the slope at 7M-perchloric acid. The ferricyanides and ferrocyanides present a more difficult problem. Both are sufficiently basic that they can be isolated as covalent acids $H_3Fe(CN)_6$ and $H_4Fe(CN)_6$ from solutions in concentrated mineral acids, the latter being obtainable from rather less concentrated acids presumably because of the greater basicity of ferrocyanide. This shows up in dilute acid media. Jordan and Ewing [6] have found the first two pK_a values for ferrocyanide to be 4·35 and 2·57 but were unable to detect the third protonation. Similarly they were unable to detect any protonation of ferricyanide. However their method, by use of a glass electrode, was only suitable for relatively dilute solutions of mineral acids. We have obtained [7] kinetic evidence that suggests that the third pK_a for ferrocyanide is *ca.* −2·2, and we have observed the precipitation of what appears to be $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ from 7·95 and 9·1M-perchloric acid respectively. This shows that these species must be present in significant amounts. However with four unknown pK_a values, together with the problem of not knowing what is the most suitable type of acidity function for these bases, it does not seem possible to account quantitatively for the variation in K with mineral acid concentration. Qualitatively we suggest that the steep rise in K up to 7M-perchloric acid is due to increasing protonation of ferrocyanide, while the fall off at higher acidities is due to protonation of ferricyanide and to increasing ionisation of molecular nitrous acid to the nitrosonium ion. However the chemistry of ferricyanide and ferrocyanide in such strongly acid media has not been investigated to any great extent.

[3/1573 *Received, 25th July,* 1973]

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[7] J. C. Bates, K. M. Davies, and G. Stedman, unpublished work.