Reaction of Nitrogen Dioxide with Ferricyanide

By K. M. DAVIES and G. STEDMAN*
(*Department of Chemistry, University College of Swansea, Swansea*)

WE have examined the kinetics of the conversion of the ferricyanide ion to nitroprusside in 6M-nitric acid at 25°. The reaction was catalysed by nitrous acid, apparently occurring through nitrogen dioxide.

The reaction was followed by direct spectrophotometry, and showed three distinct parts. On mixing the reactants there was a rapid decrease in absorbance of the peak at 420 mμ, characteristic of ferricyanide, to about 75% of its initial value;

this change took 1—2 min. During the next 10 min., the peak at 420 mμ disappeared and was replaced by one at 382 mμ, $\epsilon = 960$; during this change an isosbestic point was observed at 398 mμ. The final change involved a slow disappearance of the peak at 382 mμ following the rate law $-\mathrm{d}D/\mathrm{d}t = k_1D$, where D is the absorbance at the maximum; k_1 is 0·0165 min.$^{-1}$, and is independent of acidity, ionic strength, and nitrous acid concentration.

The reaction was also followed by the disappearance of ferricyanide (iodometry) and of nitrous acid (colorimetry), and followed the rate law $v = k_2[\mathrm{Fe(CN)_6^{3-}}][\mathrm{HNO_2}]^{\frac{1}{2}}$, with a stoicheiometry $\Delta[\mathrm{Fe(CN)_6}^{3-}]/\Delta[\mathrm{HNO_2}] = 2$. This rate law corresponds to the *second* spectrophotometric change mentioned above; iodometric analysis shows that all the ferricyanide has disappeared long before the peak at 382 mμ begins to decay significantly. The rate constant k_2 increases approximately with the third power of the stoicheiometric nitric acid concentration, and is 1·33 l.$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min.$^{-1}$ in 6M-nitric acid at 25° (ferricyanide analysis). Rate measurements in sulphuric acid with lower concentrations of nitric acid show that the complete rate law is

$$v\ (\mathrm{l.^{-1}mole\ min.^{-1}}) = 0{\cdot}0049[\mathrm{Fe(CN)_6^{3-}}][\mathrm{HNO_2}]^{\frac{1}{2}}[\mathrm{nitrate}]^{\frac{1}{2}}\,h_-^{\frac{1}{2}}$$

The change in the spectrum during the first 1—2 minutes is due to the establishment of the equilibrium

$$2\,\mathrm{Fe[CN]_6^{3-}} + \mathrm{HNO_2} + 2\,\mathrm{H^+} + \mathrm{H_2O} \rightleftharpoons 2\mathrm{Fe(CN)_6H_2^{2-}} + \mathrm{HNO_3}$$

The ferrocyanide ion is written as the doubly protonated species in view of its known basicity.[1] The equilibrium was studied spectrophotometrically in perchloric acid with very low concentrations of nitric acid. The conversion of ferricyanide into nitroprusside is slow under these conditions and the equilibrium can be studied without the concurrent reaction present in nitric acid. We find $K = [\mathrm{Fe(CN)_6H_2^{2-}}]^2[\mathrm{HNO_3}]/[\mathrm{Fe(CN)_6^{3-}}]^2[\mathrm{HNO_2}]$ is 6 and 100 in 5·5 and 6M-perchloric acid respectively, 25°. Precipitation with silver nitrate gave a solid whose i.r. spectrum was very similar to authentic silver ferrocyanide. The spectrophotometric behaviour is similar to that of our reacting solutions in nitric acid, except that equilibrium seems to be attained much more rapidly.

The species absorbing at 382 mμ can be precipitated as the diamagnetic silver salt with a 2:1 silver to iron ratio and an i.r. spectrum very similar to authentic silver nitroprusside. Treatment of the reaction solution with excess of alkali + cyanide gives 100% yield of ferrocyanide + nitrite ion. In its general reactions it seems to be very similar to nitroprusside with two outstanding differences: (i) the absorption band at 382 mμ is absent in nitroprusside; (ii) in alkali it decomposes to ferric hydroxide + ferrocyanide under conditions where nitroprusside shows no such reaction. We consider this species to be an intermediate that decomposes unimolecularly to nitroprusside.

We suggest that an equilibrium concentration of nitrogen dioxide is reacting with ferricyanide.

$$\mathrm{H^+} + \mathrm{HNO_2} + \mathrm{NO_3^-} \underset{\text{fast}}{\rightleftharpoons}$$

$$\mathrm{H_2O} + \mathrm{N_2O_4} \underset{\text{fast}}{\rightleftharpoons} 2\,\mathrm{NO_2} \qquad (1)$$

$$\mathrm{NO_2} + \mathrm{Fe(CN)_6^{3-}} \rightarrow \text{Intermediate} \qquad (2)$$

$$\text{Intermediate} \rightarrow \mathrm{Fe(CN)_5NO^{2-}} \qquad (3)$$

The rates of the reactions in (1) are known approximately,[2] and the equilibria are established much more rapidly than our measured rates of reaction. An alternative mechanism consistent with the half-order dependence upon $[\mathrm{HNO_2}]$ is a rate-determining hydrolysis of an equilibrium concentration of ferrocyanide, as is the case in alkaline solutions.[3] This seems excluded by the fact that nitrate catalyses rather than inhibits reaction. Measurements on the hydrolysis of solutions of ferrocyanide in sulphuric acid with similar values of H_0 to 6M-nitric acid showed that this was too slow to account for our measured rates.

The final products of the reaction are reported[4] to be carbon dioxide and the ammonium ion. We find that hydrogen cyanide is not a product, even though it is stable under our conditions. We suggest that nitrogen dioxide oxidises the cyanide to cyanate, which is hydrolysed to carbon dioxide and ammonia.

(*Received, November 27th*, 1967; *Com.* 1268.)

---

[1] L. E. Sutton, "Stability Constants", *Chem. Soc. Spec. Publ.*, *No.* **17**, **1964**.

[2] P. Gray and A. D. Yoffe, *Chem. Rev.*, 1955, **55**, **1069**.

[3] F. Seel and H. Koss, *Z. Naturforsch.*, 1962, **17b**, 129.

[4] G. Brauer, "Handbook of Preparative Inorganic Chemistrv", Academic Press, New York, 1965.