An Intermediate in the Reaction between Ferricyanide and Sulphite in Aqueous Solution

By R. S. MURRAY

(Department of Chemistry, The University of Hull, Hull)

THE mechanism of the oxidation–reduction reaction between $Fe(CN)_6^{3-}$ and SO_3^{2-} continues to arouse controversy. Veprek-Siska and his coworkers[1] claim that the reaction involves the intermediate $[Fe^{III}(CN)_5SO_3]^{4-}$, with the subsequent formation of sulphate, although the reasons suggested for this have recently been questioned by Brown and Higginson.[2] Earlier discussions implied the formation of dithionate ion as a product,[3] and Swinehart[4] in discussing these alternative proposals, favours the latter, which involves an outer sphere reaction, with the formation of SO_3^- radical ions. He claims to have prepared the species $[Fe^{III}(CN)_5SO_3]^{4-}$, and finds its reactivity different to that predicted by the reaction scheme proposed by Veprek-Siska.

Since CN^- and NO^+ are iso-electronic and the existence of $[Fe(CN)_5(NOSO_3)]^{4-}$ is well established,[5] it has been suggested[4] that a species such as $[Fe^{III}(CN)_5(CNSO_3)]^{5-}$ may also exist, but to date evidence for the existence of this species has not been reported. Here is reported the detection of a species believed to be $[Fe(CN)_5(CNSO_3)]^{4-}$, which is formed as an intermediate in the reaction between $Fe(CN)_6^{3-}$ and SO_3^{2-}.

Experiments have shown that a solution containing $K_3Fe(CN)_6$ (0·001M) and Na_2SO_3 (1·0M) rapidly becomes colourless, with the loss of the characteristic ferricyanide absorption bands ($t_{\frac{1}{2}}$ = 0·75 sec. at 20°). There is, however, a subsequent slower spectral change in the region 300—350 mμ, which leads to complete conversion of the original ferricyanide to ferrocyanide. Provided constant ionic strength is maintained, the rate of this slower reaction is independent of free sulphite ion concentration over the range 0·10 to 1·0M ($t_{\frac{1}{2}}$ = 23 min. at 31·0°; and ionic strength = 1·11). It is also independent of the initial concentration of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions. The previously observed[1] retardation by this latter species occurs in the initial rapid reaction.

The reaction of the intermediate solution from which excess sulphite ion has been precipitated, with H_2O_2, clearly shows the existence of two distinct species, although other experiments have shown that this solution is diamagnetic. One half of the iron species reacts rapidly with H_2O_2 at pH 2·5 giving $Fe(CN)_6^{3-}$, whereas the conversion of the remainder to $Fe(CN)_6^{3-}$ is slower and is comparable in rate to the decomposition reaction of the intermediate in the absence of H_2O_2, under the same conditions of temperature and pH. Comparative runs with $K_4Fe(CN)_6$ and H_2O_2 showed that $Fe(CN)_6^{4-}$ is rapidly oxidized to $Fe(CN)_6^{3-}$ under these conditions, and although the complexities of this reaction[6] make direct comparisons difficult, it is felt that the more reactive component of the intermediate solution is $Fe(CN)_6^{4-}$. Furthermore it would seem that the intermediate is a much poorer reductant and that decomposition to $Fe(CN)_6^{4-}$ may precede its oxidation to $Fe(CN)_6^{3-}$.

Electrophoretic analysis of the reaction products has shown that the ratio $SO_4^{2-}/S_2O_6^{2-} \geqslant 12$, in agreement with Veprek-Siska.

The results of experiments performed in the presence of nitrosobenzene have eliminated the possibility of the formation of $[Fe(CN)_5OH_2]^{3-}$, either in the formation of the intermediate, or in its subsequent decomposition reaction. Recent experiments[7] with $C^{14}N^-$ have shown that there is no exchange of the cyano-ligands of $Fe(CN)_6^{3-}$ with free cyanide ion, in the reduction reaction with sulphite.

The following reaction scheme is envisaged for the reaction between $Fe(CN)_6^{3-}$ and SO_3^{2-}:

$$(1)\quad [Fe(CN)_6]^{3-} + SO_3^{2-} \overset{\text{slow}}{\rightleftarrows} [Fe(CN)_5(CNSO_3)]^{5-}$$

$$(2)\quad [Fe(CN)_5(CNSO_3)]^{5-} + [Fe(CN_6)]^{3-} \overset{\text{rapid}}{\rightleftarrows} [Fe(CN)_5(CNSO_3)]^{4-} + [Fe(CN)_6]^{4-}$$

$$(3)\quad [Fe(CN)_5(CNSO_3)]^{4-} + H_2O \xrightarrow[\text{slow}]{\text{very}} Fe(CN)_6^{4-} + SO_4^{2-} + 2H^+$$

It is thus suggested that the redox reaction is completed by the formation of the intermediate, $[Fe(CN)_5(CNSO_3)]^{4-}$, and the subsequent very slow step is a hydrolysis reaction. This is confirmed by the magnetic measurements, and would explain the observation that the rate of decomposition of the intermediate is independent of the concentration of free sulphite ion.

It would seem likely that the sulphite ion adds to the carbon atom of a cyano ligand of $[Fe(CN)_6]^{3-}$, by analogy with the SO_3^{2-}–$[Fe(CN)_5NO]^{2-}$ reaction,[8] and it is expected that n.m.r. studies on the intermediate will give further insight into this aspect of the work.

It would seem that the formation of similar intermediates in reactions, involving other metal cyano-complexes and reductants, may be more important than hitherto expected. Already there is kinetic evidence for the formation of intermediate species in the reaction between $Fe(CN)_6^{3-}$ and NO_2^-,[9] and preliminary investigations indicate that the reaction between $Fe(CN)_6^{3-}$ and I^- may proceed, at least in part, *via* a rapidly formed intermediate.

The author gratefully acknowledges the encouragement and advice he has received from Professor W. C. E. Higginson.

(*Received, May 6th*, 1968; *Com.* 556.)

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