946. *The Radiolysis of Ferro- and Ferri-cyanide Solutions.*

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The oxidation of potassium ferrocyanide in dilute sulphuric acid solution by γ-radiation has been investigated and compared with that of ferrous sulphate. There are significant differences between the two systems, but these can be accounted for.

THE decomposition of water by ionising radiation may be represented formally as:

$$H_2O \rightsquigarrow H\cdot, \cdot OH, H_2, H_2O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By the addition of suitable scavengers, it has been possible to determine the yields of both radical and molecular products.[1] The majority of such studies however, have been carried out in acid solution and particularly in 0·4M-sulphuric acid. It is known that at higher pH, the molecular yields increase,[2] *e.g.*, $G(H_2)$ increases from 0·40 at pH 0·4 to 0·45 at pH 5, but little is known about the effect of pH on the radical yields. It has been shown from studies on the oxidation of ferrous sulphate solution[3] that $G(H)$ decreases slightly with pH, but such considerations are necessarily limited to pH < 3.

It seems desirable to measure the effect of pH on the same system over the whole range of pH. The choice of a suitable scavenger is severely restricted through considerations of solubility and stability and because it is preferable that there should be no effect of pH on it.

In view of the vast amount of work done on the ferrous sulphate system, it was decided to investigate the ferro–ferricyanide system, since this ought to be amenable to investigation over the whole pH range. Little attention has yet been paid to this system. Fricke and Hart[4] observed that in deaerated acid solution ferrocyanide was oxidised to ferricyanide by *X*-rays with $G[Fe(CN)_6^{3-}] \sim 1$. More recently,[5] it has been shown that, whereas ferrocyanide is oxidised in aerated acid solution, ferricyanide is reduced at pH > 11. However, no mechanism was put forward to account for these observations.

The present paper reports further studies on the oxidation in acid solution. An understanding of this system was necessary before extending the work to higher pH, and the effect of high pH is at present under investigation.

EXPERIMENTAL

Water from a Manesty still was distilled from alkaline permanganate and then from dilute sulphuric acid. Chemicals used were of "AnalaR" grade. Solutions of potassium ferrocyanide were made up freshly as required and, as much as possible, were kept in the dark. Solutions were aerated before irradiation by shaking them in air. Oxygenation of the solution was effected by bubbling through the solution oxygen which had been previously saturated with water vapour. Solutions were deaerated either by evacuation or by bubbling oxygen-free nitrogen through the solution.

The irradiation source was described earlier.[6] Samples (25 ml.) of solution were irradiated with γ-radiation from a 100 c ^{137}Cs source at a dose rate of 10^{16} ev ml.$^{-1}$ min.$^{-1}$, as determined by the Fricke dosimeter. The oxidation of ferrocyanide was followed by colorimetric measurement of the ferricyanide formed. Measurements were made with an Eel absorptiometer and filter 601; this gave maximum transmission at 420 mμ which is the absorption maximum of ferricyanide. At this wavelength the absorption of ferrocyanide was negligible.

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[1] Allen "The Radiation Chemistry of Water and Aqueous Solutions," Van Nostrand, New York, 1961, ch. 4.

[2] Schwarz, Losee, and Allen, *J. Amer. Chem. Soc.*, 1954, **76**, 4693.

[3] Rothschild and Allen, *Radiation Res.*, 1958, **8**, 101.

[4] Fricke and Hart, *J. Chem. Phys.*, 1935, **3**, 596.

[5] Tarrago, Meari, and Lefort, *Compt. rend.*, 1957, **344**, 244.

[6] Dobson and Hughes, *Trans. Faraday Soc.*, 1961, **57**, 1117.

Hydrogen peroxide was known to be one of the products of the radiolysis and some measurements were made on its reaction with ferrocyanide. For 10^{-2}M-ferrocyanide and at concentrations of hydrogen peroxide to be expected in the radiolyses, it was shown that the reaction

$$H_2O_2 + 2Fe(CN)_6^{4-} \longrightarrow 2Fe(CN)_6^{3-} + 2OH^- \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

was stoicheiometric and complete within 4 hr. This is in contrast with the report by Tarrago *et al.*[5] that under their experimental conditions the quantity of ferrocyanide oxidised was small compared with the quantity of hydrogen peroxide decomposed. The optical densities of solutions after irradiation were followed for this period of time, and it was confirmed that post-irradiation oxidation of ferrocyanide was complete within this period and may thus be attributed to the reaction between ferrocyanide and hydrogen peroxide. For 10^{-3}M-ferrocyanide, reaction with hydrogen peroxide was again stoicheiometric but required 18 hr. for completion. Oxidation yields reported in this work refer to complete reaction of the hydrogen peroxide formed during the radiolysis.

RESULTS AND DISCUSSION

Results for 1·0M- and 0·4M-sulphuric acid are shown in Fig. 1. The production of ferricyanide is linear with dose. The oxidation yield is independent of acidity in this concentration range and of ferrocyanide concentration in the range 10^{-3}—10^{-2}M. There is no effect of increasing oxygen concentration from aerated to oxygenated solution. However, the oxidation yield is very much reduced in deaerated solution and falls off more rapidly with dose.

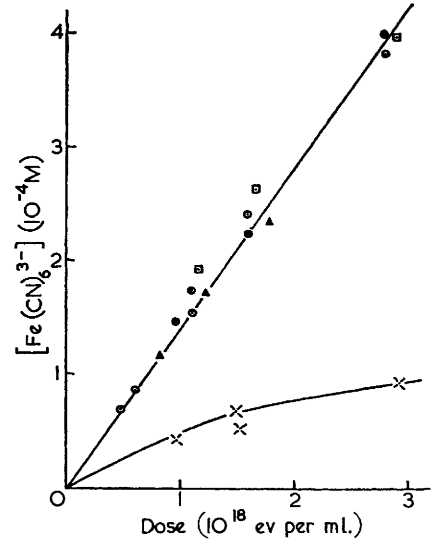

FIG. 1. Oxidation of $K_4Fe(CN)_6$ in acid solutions. All 10^{-2}M-$K_4Fe(CN)_6$ and 0·4M-H_2SO_4, except points △ and ☐ which are for 10^{-3}M-$K_4Fe(CN)_6$ and 1·0M-H_2SO_4, respectively; ○, ☐, △ aerated; ● oxygenated; × deaerated.

$G[Fe(CN)_6^{3-}]$ in aerated 0·4M-sulphuric acid is 8·3. This is very much less than the corresponding yield in the ferrous sulphate system where $G(Fe^{3+})$ is 15·5. However, since the yield is independent of ferrocyanide concentration and of dose, this lower yield cannot be attributed to back-reactions of the product ferricyanide. By analogy with the ferrous sulphate system,[7] oxidation of ferrocyanide may take place by the reactions:

$$Fe(CN)_6^{4-} + \cdot OH \longrightarrow Fe(CN)_6^{3-} + OH^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

$$Fe(CN)_6^{4-} + H_2O_2 \longrightarrow Fe(CN)_6^{3-} + OH^- + \cdot OH \quad . \ . \ . \ . \ . \ . \ . \quad (4)$$

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[7] Allen and Rothschild, *Radiation Res.*, 1957, **7**, 591.

If the HO_2 radical, which is believed to be formed in the radiolysis of aerated solutions by the reaction

$$H\cdot + O_2 \longrightarrow \cdot HO_2\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

reacted with ferrocyanide, *viz.*:

$$HO_2\cdot + Fe(CN)_6^{4-} \longrightarrow HO_2^- + Fe(CN)_6^{3-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

then, as in the ferrous sulphate system, the oxidation yield would be given by:

$$G[Fe(CN)_6^{3-}] = 3G(H) + G(OH) + 2G(H_2O_2) = 15{\cdot}5$$

That $G[Fe(CN)_6^{3-}]$ is appreciably less than this, indicates that reaction (6) does not take place. This is somewhat surprising since, from its redox potential, ferrocyanide ought to be a more powerful reducing agent. Moreover, if the oxidation by $HO_2\cdot$ involved a simple electron transfer, one would expect the oxidation of ferrocyanide to take place more readily than that of free ferrous ion, since there is little change in configuration between ferro- and ferri-cyanide.[8]

The lower yield of ferricyanide cannot be attributed to the reaction

$$H\cdot + Fe(CN)_6^{3-} \longrightarrow H^+ + Fe(CN)_6^{4-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

competing with reaction (5) since the yield is independent of oxygen concentration in the range from aerated to oxygenated solution. The reaction

$$H\cdot + Fe(CN)_6^{4-} + H^+ \longrightarrow H_2 + Fe(CN)_6^{3-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

may be excluded since, as is discussed below, results in deaerated solution indicate that this reaction does not readily take place. It appears then that the probable fate of the hydrogen atoms formed during the radiolysis is the formation of $HO_2\cdot$ radicals followed by dimerisation of these radicals:

$$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

with subsequent thermal reaction of the hydrogen peroxide produced with the ferrocyanide. Under these conditions, the oxidation yield is given by:

$$G[Fe(CN)_6^{3-}] = G(H) + G(OH) + 2G(H_2O_2) = 8{\cdot}2$$

on current values of the radical yields. This is in good agreement with the observed value.

On the above mechanism, the only reaction leading to rapid oxidation of ferrocyanide during the radiolysis is that by the $\cdot OH$ radical, namely, (3). All other oxidation proceeds by the slower thermal reaction with hydrogen peroxide. If the oxidation yield could be measured before significant reaction of the hydrogen peroxide, then the initial oxidation yield would be given by $G_i[Fe(CN)_6^{3-}] = G(OH) = 2{\cdot}9$. An attempt was made to measure the oxidation yield immediately after radiolysis. A solution of 10^{-3}M-ferrocyanide in air-saturated 0·4M-sulphuric acid was irradiated for 100 minutes. Immediately after the radiolysis, $G[Fe(CN)_6^{3-}]$ was 3·8, but it increased to a constant value of 8·2 on storage overnight. During the radiolysis, there would be some slight oxidation of the ferrocyanide, at least by molecular hydrogen peroxide, so that this measured yield is greater than the initial yield. It appears probable then that $G_i[Fe(CN)_6^{3-}]$ has about the expected value. This low value of the initial oxidation yield indicates that, whatever the mechanism by which hydrogen atoms ultimately lead to oxidation of the ferrocyanide, they do not lead to an immediate oxidation. This would be consistent with formation and subsequent dimerisation of $HO_2\cdot$ as in reaction (10), followed by thermal oxidation by the hydrogen peroxide produced.

It is interesting that the oxidation yield observed for the deaerated ferrous sulphate

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[8] Libby, *J. Phys. Chem.*, 1952, **56**, 863.

system[9] is also 8·2. In this system, oxidation by hydrogen atoms may take place by reaction (9), *i.e.*, only one ferrous ion is oxidised per hydrogen atom, in contrast to three in the aerated case. Similarly, in the aerated ferrocyanide system, in so far as two $HO_2\cdot$ radicals give rise to only one molecule of hydrogen peroxide, one ferrocyanide ion is oxidised per hydrogen atom.

That the oxidation yield is independent of acidity in the range 0·4—1·0M-sulphuric acid, indicates that radical yields do not change significantly over this range of acid concentration. It is likewise observed that $G(Fe^{3+})$ in the aerated ferrous sulphate system is independent of acid concentration in this range.[10]

At lower acidities, there is a fall in yield at higher doses, as shown in Fig. 2. This effect is independent of ferrocyanide concentration and cannot thus be attributed to competition of ferro- and ferri-cyanide for the products of the radiolysis. Addition of chloride ion has no effect on the yields. It is known that the radical $HO_2\cdot$ is a weak acid

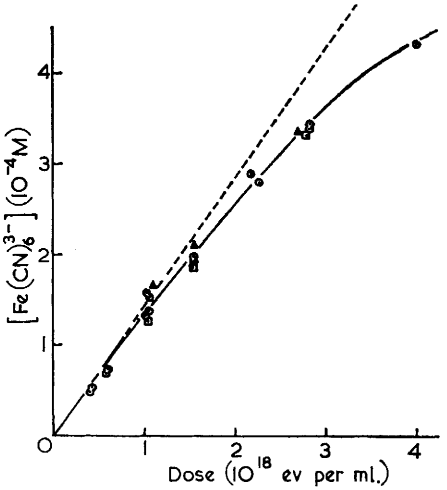

FIG. 2. Oxidation of $K_4Fe(CN)_6$ in aerated 0·05M-H_2SO_4.

○ 10^{-2}M-$K_4Fe(CN)_6$; △ 10^{-3}M-$K_4Fe(CN)_6$; ☐ 10^{-2}M-$K_4Fe(CN)_6$, 0·1M-NaCl.

Broken line shows $G[Fe(CN)_6{}^{3-}]$ = 8·3.

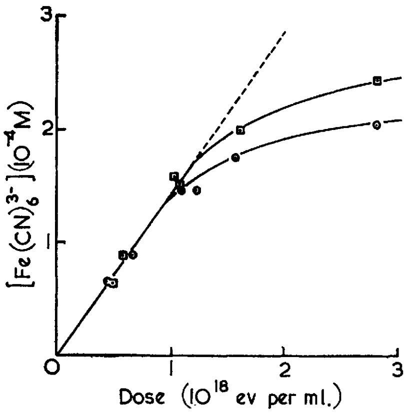

FIG. 3. Effect of methanol on oxidation of $K_4Fe(CN)_6$ in aerated 0·4M-H_2SO_4.

○ 1·0M-CH_3·OH; ☐ 0·1M-CH_3·OH.

The broken line shows $G[Fe(CN)_6{}^{3-}]$ = 8·3.

$$HO_2\cdot \rightleftharpoons H^+ + O_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

with $pK_a \sim 3$. Moreover, O_2^- is known to behave as a reducing agent. It is possible then that at higher doses, the reaction

$$O_2^- + Fe(CN)_6{}^{3-} \longrightarrow O_2 + Fe(CN)_6{}^{4-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

competes with reaction (10), leading to a lower oxidation yield. This effect would be independent of ferrocyanide-ion concentration, as is observed. At high doses, where the concentration of ferricyanide produced would be sufficient to ensure complete reaction of $HO_2\cdot$ by reactions (11) and (12), the oxidation yield would be given by:

$$G[Fe(CN)_6{}^{3-}] = G(OH) + 2G(H_2O_2) - G(H) = 0{\cdot}78$$

This is approximately the value observed by Tarrago *et al.*[5] for their limiting condition at high dose.

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[9] Rigg, Stein, and Weiss, *Proc. Roy. Soc.*, 1952, *A*, **211**, 375.
[10] Miller, *J. Chim. phys.*, 1955, **52**, 644.

Fig. 1 shows that there is a marked lowering of yield in deaerated solution and that this yield decreases at high doses. This is in agreement with the observations of Tarrago *et al.*,[5] though a post-irradiation effect attributed to molecular hydrogen peroxide was noticed, in contrast to their observations. The oxidation yield is thus very much less than in the deaerated ferrous sulphate system: $G_i[\mathrm{Fe(CN)_6}^{3-}] \approx 2{\cdot}3$. This indicates that the oxidation of ferrocyanide by hydrogen atoms (reaction 9) does not take place readily and that, particularly at higher doses, most of the hydrogen atoms produced undergo reaction (8). If the oxidising form of the hydrogen atom is H_2^+, produced in the equilibrium

$$\mathrm{H + H^+ \rightleftharpoons H_2^+} \quad \ldots\ldots\ldots\ldots \quad (13)$$

as suggested by Rigg *et al.*,[9] then it might be expected that, insofar as oxidation involves a simple electron-transfer, oxidation of ferrocyanide would take place more readily than that of the free ferrous ion. It is possible, however, that oxidation of ferrous ion by hydrogen atom involves transfer of hydrogen from the co-ordinated water of the ferrous ion:

$$\mathrm{H\cdot + H_2O,Fe^{2+},5H_2O \longrightarrow H_2 + [HO{\cdot}Fe,5H_2O]^{2+}} \quad \ldots\ldots \quad (14)$$

Insofar as the first co-ordination shell of the iron in ferrocyanide consists solely of cyanide ions, then oxidation of ferrocyanide by hydrogen atom would be more difficult. The inability of $HO_2\cdot$ to oxidise ferrocyanide, compared with its reactivity with ferrous ion, might be attributed to some similar effect. Thus, if the oxidation of ferrous ion by $HO_2\cdot$ involved a hydrogen-atom transfer mechanism:

$$\mathrm{HO_2 + H_2O,Fe^{2+},5H_2O \longrightarrow H_2O_2 + [HO{\cdot}Fe,5H_2O]^{2+}} \quad \ldots\ldots \quad (15)$$

then it might be expected that, as suggested earlier, $HO_2\cdot$ would not readily oxidise ferrocyanide.

It is interesting that it has been found [11] that hydrogen atoms produced by electrodeless discharge did not readily oxidise ferrocyanide in 0·3N-sulphuric acid.

When methyl alcohol is added to our system there is a fall in yield at higher doses, which becomes greater with increasing methanol concentration (Fig. 3). This is in contrast to the ferrous sulphate system, where the oxidation yield increases considerably with methanol concentration.[12] In this system, the enhanced yield is attributed to reactions:

$$\mathrm{CH_3{\cdot}OH + {\cdot}OH \longrightarrow {\cdot}CH_2{\cdot}OH + H_2O} \quad \ldots\ldots \quad (16)$$

$$\mathrm{CH_3{\cdot}OH + H\cdot \longrightarrow {\cdot}CH_2{\cdot}OH + H_2} \quad \ldots\ldots \quad (17)$$

$$\mathrm{CH_2{\cdot}OH + O_2 \longrightarrow {\cdot}O_2{\cdot}CH_2{\cdot}OH} \quad \ldots\ldots \quad (18)$$

$$\mathrm{{\cdot}O_2{\cdot}CH_2{\cdot}OH \longrightarrow CH_2O + HO_2\cdot} \quad \ldots\ldots \quad (19)$$

$$\mathrm{HO_2\cdot + Fe^{2+} \longrightarrow HO_2^- + Fe^{3+}} \quad \ldots\ldots \quad (20)$$

$$\mathrm{HO_2^- + H^+ \rightleftharpoons H_2O_2} \quad \ldots\ldots \quad (7)$$

$$\mathrm{H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + {\cdot}OH} \quad \ldots\ldots \quad (21)$$

The chain carriers are thought to be ·OH and $HO_2\cdot$. Insofar as the $HO_2\cdot$ radical does not oxidise ferrocyanide, no such chain processes are possible in the ferrocyanide system and the oxidation yield is not enhanced by addition of methanol. The decrease in yield at high doses may be attributed to reactions (16) and (17) followed by

$$\mathrm{{\cdot}CH_2{\cdot}OH + Fe(CN)_6^{3-} \longrightarrow CH_2O + H^+ + Fe(CN)_6^{4-}} \quad \ldots\ldots \quad (22)$$

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[11] Czapski and Stein, *J. Phys. Chem.*, 1960, **64**, 219.

[12] Dewhurst, *Trans. Faraday Soc.*, 1952, **48**, 905.

Since the number of $\cdot CH_2\cdot OH$ radicals produced by reactions (16) and (17) will increase with methanol concentration, the fall in yield will be more apparent at higher methanol concentrations. It is also possible that, at lower acidities, the hydroperoxy-radical produced by reaction (19) might reduce ferricyanide. In fact, experiments showed that irradiation of $1{\cdot}5 \times 10^{-3}$M-ferricyanide solution 1·0M in methanol in 0·05M-sulphuric acid did result in reduction of the ferricyanide.

It is apparent that there are significant differences between the ferrous sulphate and the ferrocyanide system. Nevertheless, reactions in the latter system appear to be relatively simple and suggest that this is a potentially suitable system for the study of the effect of pH on radical yields.

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