CATALYTIC OXIDATION BY MEANS OF COMPLEX IRON SALTS.

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(Received for publication, November 16, 1926.)

The observation of Manchot\(^1\) that sodium pentacyano-ammine-ferroate\(^2\) I absorbs oxygen has led Baudisch and his coworkers\(^3\) to study the catalytic action of this salt, as well as of its water analogue II, in the oxidation of pyrimidines and purines. The present authors have previously reported in this journal\(^4\) on the nature of the oxidation products obtained. In the present paper the problem is considered from the standpoint of the catalyst. The work has been limited to sodium-pentacyano-ammine-ferroate I because of the ready availability of this salt in a satisfactory state of purity.

\[
\begin{array}{cc}
\text{CN} & \text{NH}_3 \\
\text{CN} & \text{Fe} \\
\text{CN} & \text{CN} \\
\end{array}
\quad \text{Na}_3
\]

\[
\begin{array}{cc}
\text{CN} & \text{H}_2\text{O} \\
\text{CN} & \text{Fe} \\
\text{CN} & \text{CN} \\
\end{array}
\quad \text{Na}_3
\]

\(\text{I.} \quad \text{II.}\)

Theoretical.

In the system: water, sodium pentacyano-ammine-ferroate, oxygen, organic molecule, the state of affairs may be represented by the following equations.

Catalytic Oxidation with Iron Salts

\[ H_2O \rightleftharpoons H^+ + OH^- \]  \hspace{1cm} (1)

\[ \frac{1}{2}O_2 \text{(Gas)} \]
\[ \downarrow \uparrow \]
\[ 2H^+ + \frac{1}{2}O_2 \text{(Dissolved)} + 2e^- \rightleftharpoons OH^- \]  \hspace{1cm} (2)

\[ Na_3[FeCN_5\cdot NH_3] \rightleftharpoons [FeCN_5\cdot NH_3]^- + 3Na^+ \]  \hspace{1cm} (3)

\[ [FeCN_5\cdot NH_3]^- \rightleftharpoons [FeCN_5\cdot NH_3]^{2-} \]  \hspace{1cm} (4)

\[ \frac{1}{2}O_2 \text{(Gas)} \]
\[ \downarrow \uparrow \]
\[ (2) + (4) \]
\[ H^+ + \frac{1}{2}O_2 \text{(Dissolved)} + 2[FeCN_5\cdot NH_3]^{2-} \rightleftharpoons OH^- + 2[FeCN_5\cdot NH_3]^{3-} \]  \hspace{1cm} (5)

Equation 2 represents the tendency of hydrogen ion to react with dissolved oxygen, taking up 2 electrons to form hydroxyl ion. Equation 4 indicates the tendency of the complex ferroate ion to give up 1 electron to become the ferriate ion, while Equation 5, which combines Equations 2 and 4, sums up the reactions involved. Though Equation 5 is actually not reversible yet it becomes so in the presence of an oxidizable organic compound such as a pyrimidine, which can act as an acceptor for the oxygen theoretically capable of being liberated. Since, moreover, the oxidation of the pyrimidine is certainly not reversible, the ferrate ion produced by the forward process of Equation 5 is continuously reduced to the ferroate ion by the pyrimidine present so that the complex ion, therefore, acts as an oxygen carrier or oxidation catalyst.\(^5\)

**Apparatus.**

The course of the catalyzed oxidations represented in the accompanying charts was followed by measuring the oxygen absorbed. The Van Slyke amino apparatus\(^6\) was adapted to this purpose. At the beginning of an experiment the apparatus was completely filled with water. By adjusting the stop-cocks properly the excess of water in vessel \(A\) was allowed to run out. The leveling bulb was lowered and about 65 cc. of oxygen passed

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from a reservoir into burette $F$, which was then turned, and the leveling bulb raised above the apparatus. The compressed gas in the burette was now allowed to force out through stop-cock $d$ the water contained in the vessel $D$. By this means the water originally in the apparatus was displaced by oxygen. Lowering the leveling bulb until the gas in the apparatus was below atmospheric pressure allowed solutions or suspensions to be drawn into the deaminizer $D$ from its burette $B$. The volume of $D$ having previously been found, the total volume of gas in the apparatus at any moment during an experiment was determined by reading the level of the water in burette $F$.

In the experiments described the volume of solution used was 20 cc. A suspension of the organic compound in 10 cc. of buffer solution was first introduced, followed by 10 cc. of a solution of proper concentration of the iron salt, prepared just before use in an evacuated test-tube. The shaker was operated at 500 strokes per minute. The temperature was 20°C. ($\pm 2^\circ$) and the pressure 760 mm. ($\pm 10$ mm.). The volumes recorded in the figures are of moist oxygen reduced to standard conditions.

The buffer solutions employed were made up so that each 100 cc. contained: for pH 2, 9.8 gm. of $\text{H}_2\text{PO}_4 + 9.1$ gm. of $\text{KH}_2\text{PO}_4$; for pH 7, 7.1 gm. of $\text{Na}_2\text{HPO}_4 + 4.5$ gm. of $\text{KH}_2\text{PO}_4$; for pH 12, 9.5 gm. of $\text{Na}_3\text{PO}_4 + 0.4$ gm. of $\text{KH}_2\text{PO}_4$.

**DISCUSSION OF RESULTS.**

As is seen from Equation 5 the oxidation of the pentacyano-ammime-ferroate ion by elementary oxygen involves hydrogen ion. It is, therefore, to be expected that the rate of oxidation of the complex ion will be dependent on the hydrogen ion concentration. That this rate is actually inversely proportional to the pH of the solution is seen in Fig. 1.

It is also a consequence of Equation 5 that aside from other considerations the rate of reduction of the complex ferrate ion will be dependent on the hydroxyl ion concentration; that is to say, directly proportional to the pH. The ability of the pentacyano-ammime-ferroate ion to act as an oxygen carrier depends not only on the rate of oxidation of the complex ferroate ion by elementary oxygen, but also on the rate of reduction (in the presence of some
organic compound) of the complex ferriate ion (essentially the oxidation potential of the ferriate-ferroate mixture). Since these two rates are oppositely affected by the pH of the solution, it follows that what might be called the rate of oxygen carriage will have a maximum at some pH from which it will fall off on either side. These relations may be illustrated schematically as in Fig. 2.

Besides the variation of oxygen carriage power with pH must also be considered the change of oxidizability or the "apparent
Fig. 3. The catalyzed oxidation of hydantoin is more rapid at pH 12 than at pH 7.
In each experiment, 10 millimols of hydantoin were suspended in 20 cc. of buffer solution containing 1 millimol of sodium pentacyano-ammine-ferroate. Curve 1, pH 12; Curve 2, pH 7; Curve 3, pH 12 (without catalyst).

Fig. 4. The catalyzed oxidation of isobarbituric acid is more rapid at pH 12 than at pH 7.
In these experiments, 5 millimols of the pyrimidine were suspended in 20 cc. of buffer solution containing 1 millimol of catalyst. Curve 1, pH 1; Curve 2, pH 7; Curve 3, pH 12 (without catalyst); Curve 4, pH 7 (without catalyst).
oxidation potential" of the organic compound. At all events the pH at which oxygen carriage to a given organic compound may be optimum will not necessarily be that at which the amount of oxygen absorbed by the pentacyano-ammine-ferroate ion itself is large as it is, for example, in acid solution, but may actually occur in the alkaline range where the oxygen absorption of the complex salt itself is relatively low. As a matter of fact in the investigated cases of hydantoin III\(^7\) (Fig. 3), isobarbituric acid

![Graph](http://www.jbc.org/)

**Fig. 5.** The rate of catalytic oxidation of 5-aminouracil is proportional to the concentration of catalyst (pH 12).

In each experiment 5 millimols of the pyrimidine were suspended in 20 cc. of buffer solution which contained a varying amount of complex salt as follows. Curve 1, 2 millimols; Curve 2, 1 millimol; Curve 3, \(\frac{1}{2}\) millimol.

IV\(^9\) (Fig. 4) and aminouracil V,\(^10\) the optimum is somewhere on the alkaline side, since the rate of catalyzed oxidation is greater at pH 12 than it is at pH 7.

\[
\begin{align*}
\text{III.} & \quad \text{IV.} & \quad \text{V.} \\
\text{NH—CO} & \quad \text{NH—CO} & \quad \text{NH—CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{NH—CH}_2 & \quad \text{NH—CH} & \quad \text{NH—CH}_2 \\
\end{align*}
\]

\(^7\) Conant, J. B., *Chem. Rev.*, 1926, iii, 23.


From Equation 5 it may be seen that the rate of oxygen carriage will also be dependent on the concentration of the complex ion. This relation is amply illustrated in the case of the oxidation of 5-aminouracil represented in Fig. 5.

Fig. 6. Pentacyano-ammine-ferriate and ferroate are equally efficacious as oxygen carriers (pH 12).

Curve 1, 10 millimols of hydantoin with 1 millimol of ferrous salt. Curve 2, 10 millimols of hydantoin with 1 millimol of ferric salt. Curve 3, 5 millimols of 5-aminouracil with 1 millimol of ferrous salt. Curve 4, 5 millimols of 5-aminouracil with 1 millimol of ferric salt.

As previously stated Equation 5 is reversible only when an oxidizable organic compound is present to absorb the oxygen involved. This is borne out experimentally by the fact that when sodium pentacyano-ammine-ferriate is tested, as the corresponding ferrous salt previously was in pH 2, 7, and 12 (see Fig. 1) it neither evolves nor absorbs oxygen.
Since the cycle of reactions postulated above for the mechanism of the oxygen carrier action of sodium pentacyano-ammine-ferroate involves, in one stage, the reduction of the complex ferriate ion (Equation 5), essentially the same catalytic action should be exhibited by the ferriate salt as by the ferroate salt. That this condition is fulfilled is demonstrated in Fig. 6 in the cases of hydantoin and 5-aminouracil.

**SUMMARY.**

1. Pentacyano-ammine-ferroate ion is oxidized by elementary oxygen at a rate which is inversely proportional to the pH of the solution.

2. In the cases studied the rate of catalyzed oxidation is greater in alkaline solution than in neutral.

3. In the cases studied pentacyano-ammine-ferroate and pentacyano-ammine-ferriate ions have identical catalytic activity.
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