The Kinetics of the Oxygenation of Ferrous Ion in Phosphoric Acid Containing Pyrophosphate

Thesis
by
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Abstract

The kinetics of the ferrous-oxygen reaction in an acid solution containing phosphate and pyrophosphate has been investigated. The rate law at pO_2 = 151 mm is:

$$-d(Fe^{II})/dt = k_1(Fe^{II})(H_2PO_4^-)^2 + k_2(Fe^{II})(H_2P_2O_7^{=})$$

where $k_1 = 0.96(\pm 0.04)$ moles^{-2} liters^2 hr.$^{-1}$ and $k_2 = 22.7\ (\pm 1)$ mole^{-1} liter hr.$^{-1}$ at 30°C. Sodium perchlorate is used to maintain the ionic strength at 1.0-1.1M. There is inhibition due to ferric ion. This phase of the reaction has not been investigated. It is believed that the inhibition is due to the insolubility of ferric pyrophosphate at high concentrations and to the formation of complexes at low concentrations. The following mechanism, suggested by Weiss, is consistent with the experimental results.

$$Fe^{II} + O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_2^- \cdot Fe^{III} \qquad (1,2)$$

$$O_2^- \cdot Fe^{III} \xrightarrow{k_3} Fe^{III} + O_2^- \qquad (3)$$

$$O_2^- + H^+ \longrightarrow HO_2 \qquad (4)$$

$$Fe^{II} + HO_2 \longrightarrow Fe^{III} + HO_2^- \qquad (5)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \qquad (6)$$

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + OH^- + OH \qquad (7)$$

$$Fe^{II} + OH \longrightarrow Fe^{III} + OH^- \qquad (8)$$

The rate of the reaction is given by $\frac{k_1}{k_2} k_3(Fe^{II})pO_2$. The phosphate and pyrophosphate species catalyse the reaction through complex ion formation.

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INTRODUCTION

In a recent kinetic investigation of the oxygenation of ferrous ion in phosphoric acid solution, Cher and Davidson[1] found that the rate of the reaction is first order in ferrous ion and second order in dihydrogen phosphate, ferric ion having no inhibitive effect on the rate. The rate law is:

$$-d(Fe^{II})/dt = k_1(Fe^{II})pO_2(H_2PO_4^-)^2$$

The peculiar quadratic dependence on dihydrogen phosphate would be explained if it were assumed that the actual catalysis were dihydrogen pyrophosphate, formed according to the equation:

$$2H_2PO_4^- \rightleftharpoons H_2P_2O_7^= + H_2O$$

This hypothesis stimulated the present investigation.

The influence of pyrophosphate on the oxidation of ferrous ion in solution has been observed and studied by many investigators during the past years. Spoehr[2] found that when sodium pyrophosphate was added to a solution of ferrous sulfate, the absorption of oxygen by the system was greatly increased. In a later experiment Smith and Spoehr[3] studied the kinetics of the air oxidation of ferrous sulfate in the presence of sodium pyrophosphate. Since they found that the half life, (57.5 sec.), was independent of the initial concentration of the reactants, they concluded that the reaction was first order. But in repeating the experiment while changing the rate of stirring, Lamb and Elder[4] found that the reaction rate was actually diffusion controlled under the conditions employed. They made no claims as to the order of the reaction; they only concluded that in the

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[1] Cher, M. and Davidson, N., J. Am. Chem. Soc. 77, 793 (1955)

[2] Spoehr, H. A., J. Am. Chem. Soc. 46, 1496 (1924)

[3] Smith, J. H. C., Spoehr, H. A., J. Am. Chem. Soc. 48, 107 (1926)

[4] Lamb, A. B., and Elder, L. W., J. Am. Chem. Soc. 53, 137 (1931)

presence of pyrophosphate the rate of oxidation of the ferrous sulfate solution was about 1000 times faster than in 0.1 to 3.0 molar sulfuric acid containing no pyrophosphate.

In the present investigation, the Warburg manometric technique is used. Atmospheric oxygen serves as the oxidant; its pressure being maintained approximately constant throughout the investigation. The temperature is fixed at 30°C by use of the thermostated water bath of the Warburg apparatus. Sodium perchlorate is used to make the ionic strength of the system 1.0-1.1 M. For a typical experiment, weighted quantities of ferrous ammonium sulfate and tetrasodium pyrophosphate heptahydrate are dissolved in separate buffer solutions of phosphoric acid and dihydrogen phosphate. A correction is made for the change in the hydrogen ion concentration when the tetranegative pyrophosphate goes to dihydrogen and trihydrogen pyrophosphate. In most cases this correction is small. Five milliliters of solution containing specified concentrations of ferrous ion and pyrophosphate are introduced into the Warburg cell and placed in the bath. The rate of the reaction is followed by observing the change in the height of the manometers attached to the cells.

Results

Effect of Ferrous and Ferric Concentrations

The rate of oxidation is first order in ferrous ion. This is evident from studies of the effect of varying the initial concentration of Fe^{II} at fixed pyrophosphate concentration. The results are record in Table I.

TABLE I

Effect of Fe^{II} on Reaction Rate (initial rates)

$m = -d\ln(Fe^{II})/dt$ (hr.$^{-1}$)

$(H_3PO_4) = 0.770F$ (formula weight/liter

$\mu = 1.0-1.1$ M (mole/liter)($NaClO_4$)

$pO_2 = 151$ mm.

$(Fe^{II})_o$ (F)	$(H_2P_2O_7^{=})$ (F)	m (hr.$^{-1}$)
0.0051	0.0024	0.046
0.0102	0.0024	0.041
0.0204	0.0024	0.040

The results show that the rate is constant despite a fourfold change in the initial Fe^{II} concentration. Although the reaction rate is first order in Fe^{II}, when $-\ln(Fe^{II})$ is plotted against time, the resulting plot is not a straight line, but is a curve with decreasing slope (Figure I). Because of the difficulties caused by the insolubility of ferric pyrophosphate, this phase of the reaction has not been studied. It seems reasonable that Fe^{III} should inhibit the reaction because of its strong tendency to complex pyrophosphate[5,6,7,8]. As the reaction proceeds toward completion, a white precipitate, assumed to be ferric pyrophosphate, is observed in the reaction

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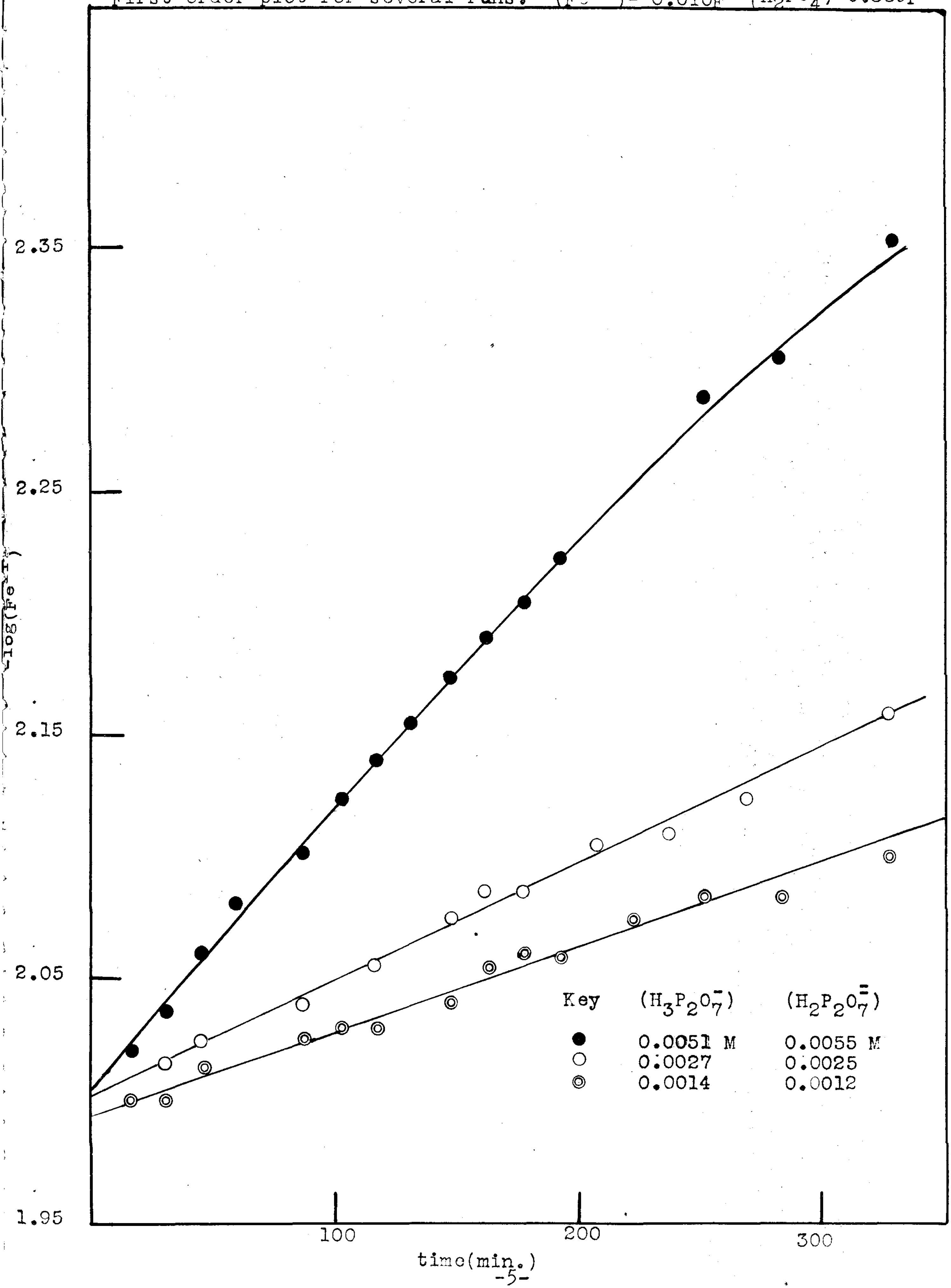
[5] Frommer, S. and Handler, W.; Z. Anorg. Allgen. Chem. 153, 135 (1926)

[6] Pascal, P. Ann. Chim. 8 16, 386 (1909)

[7] Rogers, L. B. and Reynolds, C. A.; J. Am. Chem. Soc., 71, 2081 (1949)

[8] Banergee, S., J. Indian Chem. Soc., 27, 417 (1950)

First order plot for several runs. $(Fe^{II}) = 0.010F$ $(H_2PO_4^-) = 0.389F$



vessel. In most of the experiments the precipitate was noticed after the reaction had gone to about 70°/o completion. The line drawn through the points up to about 40°/o reaction shows very little curvature. The values for the rate constants are taken from this line.

Effect of Phosphate and Pyrophosphate Concentrations

From Figure II, where the formal concentration of pyrophosphate is plotted against the rate, it is seen that the slope of the line is independent of the phosphate concentration. This indicates that there are two separate reactions taking place in the system and also that there is a linear dependence of rate on pyrophosphate concentration. The total rate expression for the reaction can be formulated as:

$$-d\ \ln(Fe^{II})/dt = k_1(Fe^{II})(H_2PO_4^-)^2 + k_2(Fe^{II})(\Sigma H_2P_2O_7^=)$$

where Σ denotes formal concentration.

Since the reactions are independent, the effect of phosphate can be studied in the absence of pyrophosphate. The results are recorded in Table II.

TABLE II

Effect of Phosphate Concentration

$(Fe^{II})_o = 0.010$ M

T = 30° C

$\mu = 1.0\text{-}1.1$ M($NaClO_4$)

$j = -d\ \ln(Fe^{II})/dt$

$pO_2 = 151$mm

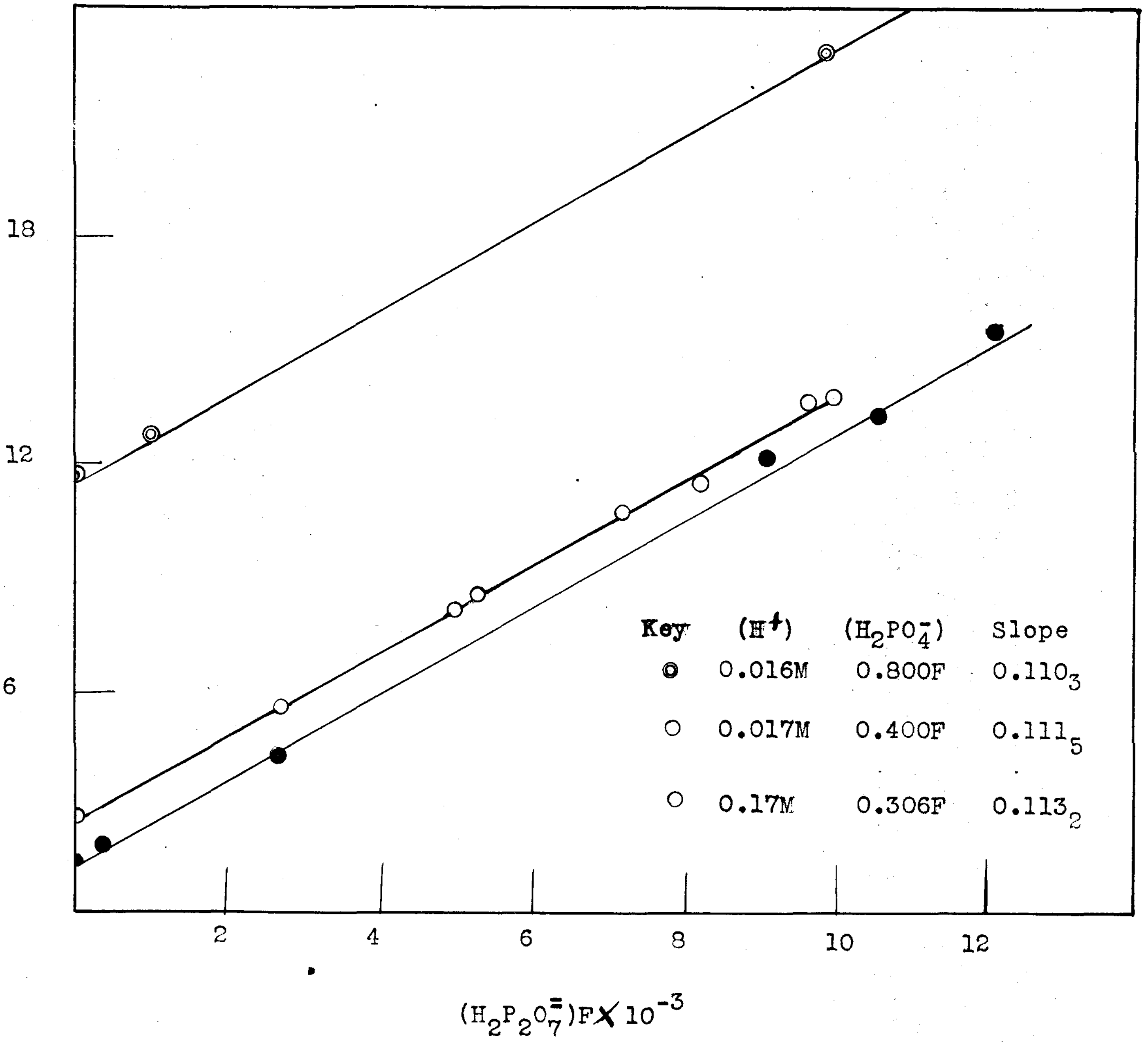
(H_3PO_4)M (calcd.)	$(H_2PO_4^-$ (calcd.)	j (hr.$^{-1}$)	$j/(H_2PO_4^-)^2$
0.559	0.121	1.52×10^{-2}	1.030
0.193	0.210	3.99 "	0.907
0.455	0.345	11.40 "	0.958

FIGURE II

Plot of rate versus formal concentration of pyrophosphate, showing the independence of the phosphate and pyrophosphate reactions.

$(Fe^{II}) = 0.010F$(formula weight/liter) $\mu = 1.0\text{-}1.1M(NaClO_4)$

$T = 30^{\circ}C$ $pO_2 = 151mm$



The data supports the fact, found by Cher and Davidson[2], that the reaction rate is second order in dihydrogen phosphate. The average value of $j/(H_2PO_4)^2$ from the Table on page 6 is in good agreement with the average value (0.9811) reported by the two investigators for pO_2 = 149 mm. Thus, in the absence of pyrophosphate, the value for k_1 is found to be 0.96(± 0.04) moles^{-2} liters^2 hr.^{-1} at 30°C and pO_2 = 151 mm.

In order to further study the effect of pyrophosphate, a value for the second mass action ionization constant for pyrophosphoric acid has to be chosen. Yost and Russell[9] quote 0.027 as the value for the ionization constant at 18°C in 1N KCl. The constant used in this investigation was obtained by using a pH meter to measure the hydrogen ion concentration of solutions containing varying amounts of $H_3P_2O_7^-$ and $H_2P_2O_7^=$, with enough $NaClO_4$ to make the ionic strength 1M. Because of the effect of perchlorate ion on the calomel electrode, it was necessary to employ a NaCl salt bridge in the determination. The pH meter, using the salt bridge, was calibrated to read 2.09 for 0.00816 M HCl in 1.00 M $NaClO_4$ at 30°C. The results are shown in Table III. The average value for the second mass action ionization constant (0.0207 moles/liter) is used in the investigation.

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[9] Yost, D. M. and Russell, H., Systematic Inorganic Chemistry (Prentice-Hall, Inc.) New York (1946) p. 228

TABLE III

The Determination of the Second Mass Action Ionization Constant of Pyrophosphate Acid

(H^+) M (moles/liter)	$(H_3P_2O_7^-)$ (calcd.)	$(H_2P_2O_7^=)$ M (calcd.)	K(ionization constant) moles/liter
9.55×10^{-3}	8.74×10^{-3}	2.18×10^{-2}	0.0239
9.12 "	9.18 "	2.13 "	0.0212
12.60 "	11.8 "	1.87 "	0.0200
12.0 "	12.4 "	1.80 "	0.0176

Dihydrogen pyrophosphate was found to be the effective catalyst by studying the rate of the reaction in the presence of varying amounts of dihydrogen and trihydrogen pyrophosphate. Because of the buffered nature of the solutions, it is difficult to vary the $H_2P_2O_7^{=}/H_3P_2O_7^{-}$ ratio without changing the concentration of $H_3P_2O_7^{-}$. But it is apparent from the results displayed in Table IV that the rate varies according to the first power of the $(H_2P_2O_7^{=})$ when the $\frac{(H_2P_2O_7^{=})}{(H_3P_2O_7^{-})}$ ratio is varied from 0.3 to 1.6. There is some scatter at low concentrations which is probably due to a small surface effect.

TABLE IV

Effect of Varying the Pyrophosphate Concentration

$(Fe^{II})_o = 0.010M$ $T = 30°C$ $\mu = 1.0\text{–}1.1$ M $(NaClO_4)$

$n = (-d\ln(Fe^{II})/dt - k_1(H_2PO_4)^2$ $pO_2 = 151$ mm $k_1 = 0.96(\pm 0.04)$

$(mole^{-2} liters^2 hr^{-1}$

(H) M (calcd.)	(H_3PO_4) M (calcd.)	$(H_2PO_4^-)$ M (calcd.)	$(H_3P_2O_7^-)$M (calcd.)	$(H_2P_2O_7^=)$M (calcd.)	n $(hr.^{-1})$	$n/(H_2P_2O_7^=)$=1 $(hr^{-1}mole)$
0.0158	0.238	0.151	0.32×10^{-3}	0.21×10^{-3}	0.0050	23.8
0.0178	0.189	0.214	1.26	1.45	0.0330	22.7
0.0729	0.557	0.153	8.40	2.55	0.0545	21.4
0.0232	0.209	0.180	2.74	2.54	0.0546	21.5
0.0138	0.164	0.239	1.93	3.10	0.0654	21.0

Since $n/(H_2P_2O_7^=)$ gives the value for k_2, it is apparent from Table IV that $k_2 = 22.7(\pm 1)$ moles^{-1} liters hr.$^{-1}$.

Effect of Surface

Cher and Davidson[2] found that there is some heterogeneous reaction due to surface but the effect of the results is small. The insignificance of the heterogeneous reaction is suggested by the good agreement between their work and the work described in this report.

DISCUSSION

The results of the investigation of the oxygenation of Fe^{II} in the presence of $H_2PO_4^-$ and $H_2P_2O_7^=$ show that the rate is first order in (Fe^{II}) and $(H_2P_2O_7^=)$

and second order in ($H_2PO_4^-$). There is a marked decrease in the rate after the reaction has reached about 70°/o completion. This decrease is attributed to Fe^{III} inhibition. The influence of Fe^{III} has not been studied. The results are in good agreement with those of Cher and Davidson[2], who studied the rate of oxidation of Fe^{II} in phosphoric acid in the absence of pyrophosphate. The present results seem to indicate that in the system studied by the two investigators, $H_2PO_4^-$ and not $H_2P_2O_7^=$ is the effective catalyst. This distinction is made in the following manner.

In an acid solution containing H_3PO_4 and $H_2PO_4^-$ dihydrogen pyrophosphate, if present, is formed by the reaction:

$$(1)\quad 2H_2PO_4^- \rightleftarrows H_2P_2O_7^= + H_2O \qquad K = \frac{(H_2P_2O_7^=)}{(H_2PO_4^-)^2} \text{ moles}^{-1} \text{ liters}$$

The kinetic results obtained in the present investigation show that the rate of the reaction due to pyrophosphate can be formulated as:

$$\text{Rate} = k_2(Fe^{++})(H_2P_2O_7^=)$$

If the value of ($H_2P_2O_7^=$), given in Equation (1), is substituted in the rate expression then,

$$\text{Rate} = Kk_2(Fe^{++})(H_2PO_4^-)^2$$

but, from the results in the absence of pyrophosphate:

$$\text{Rate} = k_1(Fe^{++})(H_2PO_4^-)_2$$

Therefore, if pyrophosphate is the catalytic species then,

$$K = \frac{k_1}{k_2} = \frac{0.96}{22.7} = 0.0423 \text{ moles}^{-1} \text{ liters}$$

However, K can be estimated from thermodynamic values for the reaction:

$$(2)\quad HPO_4^= + H_2PO_4^- \rightleftarrows HP_2O_7^= + H_2O$$

R. Powell and R. Connick (private communication to Norman Davidson) estimate the entropy for the reaction to be 3 e. u. If Sturtevant's[10] value for the heat of the reaction (5810 cal/mole) is accepted, then, a value for the equilibrium constant of reaction (2) can be obtained. From these values the equilibrium constant is 2.51 x 10^{-4} mole^{-1} liter.

If the values for the mass action ionization constants of $H_2PO_4^-$ and $H_2P_2O_7^=$ as quoted in Yost and Russell[~~10~~ 9] are used, an approximation for the equilibrium constant (K) of reaction (1) can be obtained.

$$H_2PO_4^- \rightleftarrows HPO_4^= + H^+ \qquad K' = 6.20 \times 10^{-8}$$

$$H^+ + HP_2O_7^{\equiv} \rightleftarrows H_2P_2O_7^= \qquad K'' = 3.30 \times 10^{-5}$$

$$H_2PO_4^- + HPO_4^= \rightleftarrows HP_2O_7^= + H_2O \qquad K''' = 2.51 \times 10^{-4}$$

$$2H_2PO_4^- \rightleftarrows H_2P_2O_7^{\equiv} + H_2O \qquad K = 5.15 \times 10^{-7}$$

Since the value for K as determined from thermodynamic data is much smaller than the value obtained from assuming that $H_2P_2O_7^=$ is the catalytic species, it can be concluded that, in the absence of added pyrophosphate, $H_2PO_4^-$ itself is the active catalyst in the oxygenation of Fe^{II} in the H_3PO_4 - $H_2PO_4^-$ system.

Mechanism

A series of mechanisms have been proposed for the oxidation of Fe^{II} in aqueous solution[5,11,12]. The one suggested by Weiss is as follows:

$$-d(Fe^{II})/dt = 4k'_1(Fe^{II})(O_2)\left(\frac{k'_3(Fe^{II})(H^+)}{k'_3(Fe^{II})(H+) + k'_2k_{HO_2}(Fe^{II})} \right)$$

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[10] Sturtevant, J. M. and Ging, N. S.; J. Am. Chem. Soc. 76, 2087 (1954)

[11] Abel, E. Monatshefte 82, 835 (1951)

[12] Weiss, J. Experientia 9, 61 (1953)

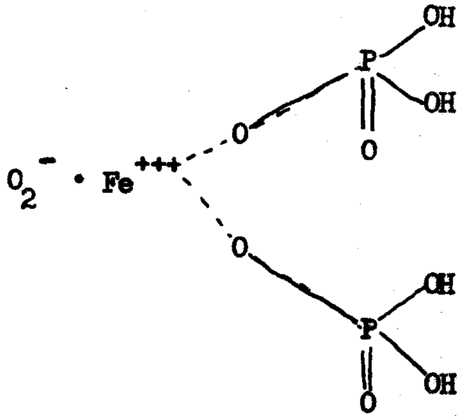
which proceeds via the sequence of one-electron oxidations as shown in the abstract.

In the present investigation the rate is found to be dependent on the anions present. Weiss postulates that the ion pair formed in the reaction,

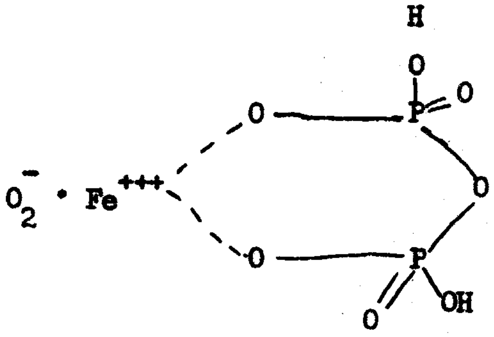
$$Fe^{II} + O_2 \rightleftarrows (Fe^{III}O^-_2)$$

is stabilized by an anion capable of complexing it. In the system considered in this report there are two different complexes. They can be formulated in the following manner.

(a) with dihydrogen phosphate



(b) with dihydrogen pyrophosphate



The fact that the complex of pyrophosphate with Fe^{III} is much stronger than the one with dihydrogen phosphate can account for the greater catalytic effect of the former.

Conclusion

The results of the present investigation support the theory that the rate of oxygenation of ferrous ion in various acid media varies as the stability of ferric ion complexes in the solution. Ferrous oxygenation has been studied in the following acid solutions: perchloride[13], sulfuric[14], hydrochloric[15], phosphoric[1,6], and pyrophosphoric. Since the rate of oxygenation of ferrous in the solutions increases in the order named, it can be predicted that the stability of the ferric complexes will increase in the same order.

A complete investigation should be made of the ferric complexes in various media. The results would aid in predicting the magnitude of the reaction rate of the oxygenation of ferrous ion in other media.

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[13] George, P., *J. Chem. Soc.*, 4349 (1954)

[14] Huffman, R. E., (private communication)

[15] McBain, J. W., *J. Phys. Chem.* *5*, 623 (1901)