for effecting reduction of nitrosamines to the hydrazines is preferred. First, the reactions can be carried out in a completely homogeneous system. Secondly, recovery of the product involves only removal of the solvent by evaporation after which the residue is subjected to either an extraction or a distillation procedure.

URBANA, ILLINOIS

[CONTRIBUTION NO. 1940 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Kinetics of the Oxygenation of Ferrous Iron in Phosphoric Acid Solution

BY MARK CHER AND NORMAN DAVIDSON

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The rate of the Fe^{++}, O_2 reaction in H_3PO_4, NaH_2PO_4 solutions at an ionic strength of 1.0–1.1 M ($NaClO_4$) has been studied by a manometric technique. The rate law is $-d(Fe^{++})/dt = k(Fe^{++})p_{O_2}(H_2PO_4^-)^2$, where $k = 4.5(\pm 0.3)$ atm.$^{-1}$ mole^{-2} liter^2 hr.$^{-1}$ at 30°. The activation energy is 20(±2) kcal. There is some heterogeneous reaction on a glass wool surface, but it is believed that the above rate data apply to the homogeneous reaction. There is no inhibition by added Fe^{+++}. A one-electron reaction mechanism with the rate-determining step, $Fe^{++} + O_2 \rightarrow Fe^{+++} + HO_2$, is consistent with the results. The marked catalytic effect of added Cu^{++} can be explained by the reactions (unbalanced with respect to H^+): $Fe^{++} + Cu^{++} \underset{k_8}{\overset{k_7}{\rightleftarrows}} Fe^{+++} + Cu^+$; $Cu^+ + O_2 \underset{k_{10}}{\overset{k_9}{\rightleftarrows}} Cu^{++} + HO_2$; $HO_2 + Fe^{++} \xrightarrow{k_3} Fe^{+++} + H_2O_2$. At 30°, $\mu = 1\ M$, $(H_3PO_4) = 0.434\ F$, $(H_2PO_4^-) = 0.302\ F$, $p_{O_2} = 150$ mm., $k_7 = 1.0 \times 10^8\ M^{-1}$ hr.$^{-1}$, $k_9/k_8 = 5.1 \times 10^{-2} M^{1}$ atm.$^{-1}$, and $k_{10}/k_3 = 23$.

In 1935, Weiss[1] suggested that the oxygenation of dipositive iron, Fe^{II}, in aqueous solution proceeds *via* the sequence of one-electron oxidations.

$$Fe^{II} + O_2 \underset{2}{\overset{1}{\rightleftarrows}} Fe^{III} + HO_2 \qquad (1,2)$$

$$Fe^{II} + HO_2 \longrightarrow Fe^{III} + H_2O_2 \qquad (3)$$

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + OH + H_2O \qquad (4)$$

$$Fe^{II} + OH \longrightarrow Fe^{III} + H_2O \qquad (5)$$

The reactions as written are not balanced with respect to hydrogen ion and are not intended to specify the dependence of reaction rate on this variable nor to distinguish between the acid, HO_2 and its anion, O_2^-. Reactions 4 and 5 are fast and not rate determining and have been independently investigated.[2,3] Until very recently, there has been no strong experimental evidence for reactions 1 and 2, but the mechanism has been widely accepted because of the evidence for the occurrence of HO_2 in other reaction systems.

The most reliable and extensive of the early studies of the oxygenation of Fe^{++} in *homogeneous* systems appear to be those by Lamb and Elder[4] and McBain[5] in which it was found that in sufficiently acid (>0.1 M) H_2SO_4 solution, $-d(Fe^{++})/dt = k(Fe^{++})^2(O_2)(H^+)^0$, suggesting that the rate-determining step is the termolecular, two-electron oxidation

$$2Fe^{II} + O_2 \longrightarrow 2Fe^{III} + H_2O_2 \qquad (6)$$

There is a preliminary announcement of a recent confirmation of this rate law.[6] The interpretation of these experiments appears to us to be valid; nevertheless, some skepticism is permissible because rather concentrated solutions ($(FeSO_4) > 0.1\ M$) were used in order to get a measurably fast reaction rate, so that the inference of kinetic order from concentration dependence is possibly uncertain because of uncertain activity effects. A brief and not entirely conclusive study in this Laboratory of the same system at higher temperatures will be reported in a following paper.[7]

It is to be expected that the rate of oxygenation of Fe^{II} can be increased by the presence of reagents that complex Fe^{III} strongly. The present paper describes a study of the Fe^{II}, O_2 reaction in H_3PO_4, $H_2PO_4^-$ solutions, in which it has been found that the reaction is much faster than in H_2SO_4 solution and apparently proceeds according to the Weiss mechanism. The catalytic effect of Cu^{++} has also been elucidated.

While our investigation was in progress, it has been announced that in concentrated hydrochloric acid[8] and in the presence of fluoride ion,[6] the Fe^{++}, O_2 reaction rate is first order in each component.

It should also be noted that, some time ago, it was discovered that the Fe^{II} oxygenation is rapid in pyrophosphate solution,[9] although the claim that the reaction is first order[9] in Fe^{II} has been criticized[4] on the grounds that the reaction rate was actually diffusion controlled under the conditions used.

Experimental

The rate of O_2 uptake was measured with a Warburg manometer apparatus (American Instrument Co. no. 5-134). The apparatus was well thermostated and had provision for vigorous shaking of the reaction mixture. The manometric technique has several advantages for reactions that do not proceed too rapidly (> *ca.* 30 minute half time); it is easy to run a large number of samples concurrently, and the method is sensitive to small amounts of reaction. The sensitivity of the manometers was

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[1] J. Weiss, *Naturwissenschaften*, **23**, 64 (1935).

[2] F. Haber and J. Weiss, *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

[3] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

[4] A. B. Lamb and L. W. Elder, THIS JOURNAL, **53**, 137 (1931).

[5] J. W. McBain, *ibid.*, **5**, 623 (1901).

[6] J. Weiss, *Experientia*, **IX**, 61 (1953).

[7] R. E. Huffman, N. Davidson and J. Andelin, manuscript to be submitted to THIS JOURNAL.

[8] A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

[9] J. H. C. Smith and H. A. Spoehr, THIS JOURNAL, **48**, 107 (1926).

0.0015 − 0.0019 mmoles of Fe^{++} oxidized (or $3 \times 10^{-4} - 4 \times 10^{-4}$ *M* Fe^{++} for the five cc. of solution used) per cm. displacement of the manometric fluid.

Reagent grade materials and conductivity water were used for all solutions, unless otherwise specified. Sodium perchlorate solution for maintaining ionic strength was made by neutralization of known amounts of 85% perchloric acid or from C.P. $NaClO_4 \cdot H_2O$ (Fisher). Weighed quantities of $Fe^{II}(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ were dissolved in the desired H_3PO_4, $H_2PO_4^-$ buffer as needed; Fe^{III} solutions (from $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$) could not be stored in such buffers because of slow precipitation of ferric phosphate and were prepared in H_3PO_4 solution. Fe^{II} solutions were freshly prepared for each run.

The procedure was to dissolve the salts in the phosphate solutions, transfer 5 ml. to a 15-ml. reaction flask, attach the flask to the manometric apparatus, and turn on the shaking mechanism. It required 3–5 minutes for vapor pressure and temperature equilibrium to be established and the initial rapid changes in pressure to cease. The pressure reading at this time was taken as that for zero reaction. For reactions in pure oxygen, the gas from a cylinder was passed in through the stopcock at the top of the manometer and out through an outlet on the side of the reaction flask. About 1/2 liter of gas was passed through the system in about five minutes. Preliminary tests showed that washing the gas by bubbling it through concentrated sulfuric acid and then water had no significant effect.

In general the starting procedure described above was satisfactory. Most of the reactions in the absence of added Cu^{++} were sufficiently slow so that, by avoiding undue contact with the air, a delay of one hour between the time of dissolving the samples and the time of taking the first reading was not serious. Such a delay often occurred when a large number of samples were being started at one time. Permanganate titrations for Fe^{II} for several typical cases showed that, as expected, the difference between the actual and calculated concentration (from weight of Mohr's salt) was 1.8% one hour after preparation of the solution.

Stopcocks and ground joints were lubricated with Apiezon grease. A large glob of grease deliberately placed in the reaction flask did not affect the reaction rate in one trial.

In order to test whether the transference of gas into the solution was rate determining, water, which had been degassed by boiling, was introduced into the cell and the shaking mechanism started. A large drop in pressure (10 cm.) corresponding to the solubility of air in water was observed within ten seconds, after which there was only the much smaller pressure adjustment for vapor pressure equilibration over a period of 3–4 minutes. It is clear that the reacting solutions were at all times saturated with gas.

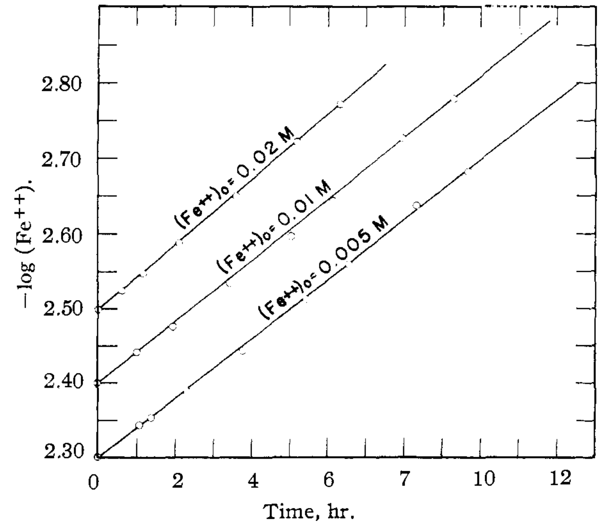

Fig. 1.—First-order plots for several reactions; 1.00 *F* H_3PO_4, 30°, p_{O_2} = 711 mm., μ = 1.0–1.1 *M* ($NaClO_4$). The vertical coördinate for $(Fe^{++})_0 = 0.0100$ *M* is $-\log (Fe^{++}) + 0.400$; for $(Fe^{++})_0 = 0.0200$ *M*, it is $-\log (Fe^{++}) + 0.800$.

Results

Effect of Fe^{II} and Fe^{III} Concentrations.—The rate of oxidation is first order in ferrous ion and independent of the ferric ion concentrations. This is evident both from the course of any one reaction with time (Fig. 1) and from studies of the effect of varying the initial concentrations of Fe^{II} and Fe^{III} at fixed O_2 pressure (Table I). In connection with Fig. 1 it should be noted that O_2 is present in excess and its partial pressure is essentially constant during any one run, decreasing by about 10% for runs in air and about 2% for runs in pure oxygen during the course of the reaction.

TABLE I

EFFECTS OF (Fe^{II}) AND (Fe^{III}) ON REACTION RATE

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

(H_3PO_4) = 1.00 *F* (formula weights/liter); μ (ionic strength) = 1.0–1.1 *M* (mole/liter) ($NaClO_4$); P_{O_2} = 711 mm.; *t* = 30.0°.

(Fe^{II})	(Fe^{III})	l, $hr.^{-1}$
(Formula wt./l.)		
0.50×10^{-2}	0	0.094
1.00	0	.096
2.00	0	.100
1.00	0.51×10^{-2}	.101
1.00	1.02	.102
1.00	2.04	.099
1.00	4.08	.097

Identification of the Phosphate Catalyst.—To investigate this phase of the problem it is necessary to make a choice for the first mass action ionization function of H_3PO_4, $(H^+)(H_2PO_4^-)/(H_3PO_4)$ mole/liter, under the conditions of the experiments (30.0°, μ = 1.0). The thermodynamic ionization constant at 30° is 0.007 mole/kilogram solvent[10]; several reported values for the mass-action ionization constant are 0.016 mole/liter (30°, μ = 0.56, KCl)[11] and 0.030 mole/liter (30°, μ = 0.665, $NaNO_3$).[12] We have chosen to measure the *p*H's of solutions containing varying amounts of H_3PO_4, NaH_2PO_4 and $NaClO_4$ with a *p*H meter calibrated to read *p*H 2.75 for 0.00177 *M* HCl, 1.00 *M* $NaClO_4$, and to compute the ionization constant to be used in each experiment. This procedure did not give particularly constant values of K_1; this result is not unexpected since the amounts of H_3PO_4 and NaH_2PO_4 are not negligible compared to the $NaClO_4$. The measured values of K_1 range from 0.019 to 0.024 and are shown in Table III; a value of 0.020 has been used for the experiments of Table II.

From the results displayed in Table II it may be seen that at constant $H_2PO_4^-$, the reaction rate is constant despite large variations in (H^+) and (H_3PO_4). *The results of Table III show that, as the $H_2PO_4^-$ concentration is varied at approximately constant (H^+), the rate varies as $(H_2PO_4^-)^2$.* There is some scatter (~20%) but no discernible systematic trend as $(H_2PO_4^-)^2$ varies by a factor of 16. Be-

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[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd edition, Reinhold Publishing Corp., N. Y., p. 580.

[11] R. Griffith and A. McKeown, *Trans. Faraday Soc.*, **36**, 776 (1940).

[12] O. Lanford and S. Kiehl, THIS JOURNAL, **64**, 292 (1942)

TABLE II

EFFECT OF VARYING (H^+) AND (H_3PO_4), $(H_2PO_4^-)$ CONSTANT

$(Fe^{II})_0 = 0.0100$ *F*; $t = 30.0°$; $\mu = 1.0\text{–}1.1$ *M* ($NaClO_4$), assume $K_1 = (H^+)(H_2PO_4^-)/(H_3PO_4) = 0.020$ *M*; $l = -d \ln (Fe^{++})/dt$ for $P_{O_2} = 713$ mm., $m = -d \ln (Fe^{++})/dt$ for $p_{O_2} = 150$ mm.

$(H_2PO_4^-)$ (*F*)	(H_3PO_4) (*F*)	(H^+) (*M*) (calcd.)	$(H_2PO_4^-)$ (*M*) (calcd.)	*l*, hr.$^{-1}$	*m*, hr.$^{-1}$
0.184	0.218	0.02	0.20	0.161	0.0414
.17	.33	.03	.20	.149	.0360
.15	.55	.05	.20	.164	.0392
.12	.88	.08	.20	.185	.0440

TABLE III

EFFECT OF VARYING $(H_2PO_4^-)$ AND (H_3PO_4), (H^+) CONSTANT

$(Fe^{II})_0 = 0.0100$ *F*; $t = 30.0°$; $\mu = 1.0\text{–}1.1$ *M* ($NaClO_4$), $l = -d \ln (Fe^{II})/dt$ for $p_{O_2} = 711$ mm.; $m = -d \ln (Fe^{++})/dt$ for $p_{O_2} = 149$ mm., (H^+) measured with *p*H meter.

$H_2PO_4^-$ (*F*)	0.368	0.276	0.184	0.092
H_3PO_4 (*F*)	.436	.327	.218	.109
(H^+) (*M*)	.025	.023	.020	.017
$(H_2PO_4^-)$ (*M*)	.393	.299	.204	.109
K_1	.024	.023	.021	.019
l (hr.$^{-1}$)	0.635	0.391	0.157	0.046
m	0.150	0.0975	0.0405	0.0106
$l/(H_2PO_4^-)_2$	4.12	4.37	3.77	3.87
$m/(H_2PO_4^-)^2$	.970	1.09	0.973	0.892

cause of the buffered nature of the solutions, the calculated molar concentrations of $(H_2PO_4^-)$ are not greatly different from the formal concentrations; therefore, uncertainties as to the value of K_1 do not affect the conclusions above. It is of course conceivable that there are small contributions to the rate corresponding to other powers of $(H_2PO_4^-)$; the results above simply show that the square term is the main one under the conditions of these experiments.

Using a value of 0.020 for K_1, the data of Table I for the rate of oxygenation in 1 *F* H_3PO_4 with $p_{O_2} = 713$ mm. may be used to calculate an average value of $l/(H_2PO_4^-)^2$ of 5.7, compared to the value of 4.0 for the NaH_2PO_4, H_3PO_4 buffers. The cause of this discrepancy is presumably related to the marked differences in the two reaction media, but is not known in detail. The experiments summarized by the data in the first three rows of Table II give values of $l/(H_2PO_4^-)^2$ or $m/(H_2PO_4^-)^2$ that agree with those of Table III, but the values of these quantities, 4.63 and 1.10, for the experiments in the fourth row (0.12 *F* $H_2PO_4^-$, 0.88 *F* H_3PO_4) are high; it may be that high concentrations of phosphoric acid affect the viscosity and other physical properties of the medium and thereby affect the rate.

Effect of Oxygen and of Surface.—Examination of the data already presented, as well as those of many other experiments that were performed but are not tabulated here, reveals that the ratio of apparent first-order rate constants, $-d \ln (Fe^{++})/dt$, in oxygen and air are about 4:1 instead of 4.76:1 as expected for first-order dependence on p_{O_2}. Results obtained with various mixtures of nitrogen and oxygen are shown in Fig. 2. Above $p_{O_2} \cong 100$ mm., the data fall on a straight line with a positive intercept, so that the extrapolated reaction rate at zero oxygen pressure is about 21% of the rate in air ($p_{O_2} = 150$ mm.). The data at low pressures are not sufficiently accurate to reveal whether the rate constant curves down smoothly to zero at zero oxygen pressure or whether the linear behavior obtains even at very low oxygen pressures.

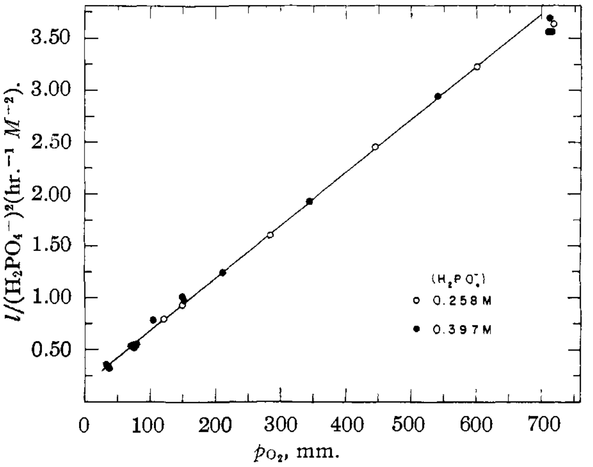

Fig. 2.—Dependence of rate upon oxygen pressure; $(Fe^{++})_0 = 0.0100$ *M*, 30°: ●, $(H_3PO_4) = 0.430$ *F*, $(H_2PO_4^-) = 0.370$ *F*; ○, $(H_3PO_4) = 0.271$, $(H_2PO_4^-) = 0.233$ *F*.

Rate measurements with added glass wool were performed in order to investigate possible surface catalytic effects. Pyrex glass wool was baked in an oven at 200° for 3–4 hours in order to eliminate organic contaminants. The surface area of the glass fibers was estimated from the diameter of the fibers (8×10^{-4} cm.) and the density of glass (2.2 g./cc.) as 2300 cm.^{2}/g. The surface area of the reaction flasks is about 50 cm.^{2} The flasks were cleaned, just as in all our experiments, by allowing them to stand with cold concentrated sulfuric acid for 24 hours and rinsing copiously with water.

The results, presented in Table IV, have been analyzed by assuming that *l* (observed rate) $= p + qS$, where *S* is the surface area, and *p* and *q* are rate constants for the homogeneous and surface reactions, respectively. The values of *p* and *q* obtained from each successive pair of points are listed. The linear relation works fairly well, and it appears that the activity of the glass wool is proportional to its surface area. It is clear that if the surface of the Pyrex reaction flask is no different from the surface of the Pyrex glass wool, the contribution of the surface reaction is rather small for the reactions in the absence of glass wool. There is, of course, no compelling evidence that the surface reactivities of the flask surface and the glass wool are nearly alike, but this conclusion seems to us to be very probable. If the flask surface were much more reactive than the glass wool, this could be due only to impurities adsorbed on the surface. The reaction rates would then be expected to vary from flask to flask and from day to day. The fact that the results are reasonably reproducible, coupled with the observed effects due to baked out glass wool, strongly supports the conclusion that the reaction rates observed in the absence of glass wool are principally due to homogeneous reaction. It is pertinent to recall at this point that added stopcock grease does not affect the reaction rate.

TABLE IV

EFFECT OF SURFACE AREA

$(Fe^{++})_0 = 0.00994$, $(H_2PO_4^-) = 0.233$ F, $(H_3PO_4) = 0.250$ F, $t = 30.0°$, $l = -d \ln (Fe^{++})/dt$.

p_{O_2} (mm.)	Wt. of glass wool (g.)	Surface area (cm.^{2})	l (hr.$^{-1}$)	p (hr.$^{-1}$) $\times 10^2$	$50\ q$ (hr.$^{-1}$) $\times 10^3$
150	0	50[a]	0.0690	6.53	3.7
150	0.324	790	.123	6.02	4.0
150	1.804	4200	.394		
715	0	50[a]	.253	24.8	5.4
715	0.535	1300	.389	26.0	5.0
715	1.775	4100	.667		

[a] Surface area of reaction cell.

We return now to a consideration of the effects of oxygen pressure. According to Table IV, the heterogeneous rate is not very dependent on pressure. However, the homogeneous rates in air and oxygen are essentially in the ratio of 1:4, rather than 1:4.76. The straight line plot of Fig. 2 indicates that the pressure independent term in the reaction rate is about 21 and 6% of the total rate in air and oxygen, respectively; whereas, according to Table IV, the heterogeneous rate is about 6 and 2% of the homogeneous rate in air and oxygen, respectively. Therefore, the pressure independent reaction rate is not principally due to heterogeneous reaction.

An effort was made to measure the reaction rate at 1.5 atm. pressure of oxygen in a round-bottom 25-ml. flask closed by a stopcock. The flask containing the Fe^{++} solution and the high pressure oxygen was agitated in the thermostat for a specified time (~40% reaction) and the remaining Fe^{++} determined by titration. The specific rate constants so obtained were about 50% too high, for which we can offer no explanation.

It is obvious that the results of this section are quite unsatisfactory in that there are some unexplained effects of pressure on reaction rate and some undiscovered sources of irreproducibility of the experiments. We have endeavored to expose these difficulties fully in the discussion above. With the time and techniques available for these experiments, we have not been able to discover the causes of these difficulties. However, we believe that, in view of the over-all consistency and reproducibility of the results reported in the preceding and following sections, it is reasonable to provisionally accept the conclusion that the main part of the reaction studied here is a homogeneous reaction with a rate proportional to the partial pressure of oxygen and that this rate is an intrinsic property of the Fe^{++}, H_3PO_4, O_2 system and not principally due to traces of impurities.

Effect of Temperature.—Table V lists the results of a set of experiments on the temperature coefficient of the reaction. The activation energy is 20 (±2) kcal. It may be noted that the temperature coefficient of the ionization constant of phosphoric acid is very small[10]; the concentration of $H_2PO_4^-$ is essentially constant and independent of temperature in the buffered solutions used.

TABLE V

EFFECT OF TEMPERATURE

$(H_3PO_4) = 0.440$ F, $(H_2PO_4^-) = 0.377$ F, $p_{O_2} = 150$ mm., $l = -d \ln (Fe^{++})/dt$, $\mu = 1.0\text{–}1.1$ M $(NaClO_4)$.

$(Fe^{++})_0$, F $\times 10^2$	t, °C.	l, hr.$^{-1}$	ΔH_{act}, kcal.
0.998	30.0	0.172	
0.998	30.0	.167	18.4
1.06	25.0	.103	
1.06	25.0	.100	22.1
1.06	20.0	.055	
1.06	20.0	.054	
1.06	20.0	.053	

Catalytic Effects Due to Cu^{++}.—In view of the interesting effects of cupric ion as a catalyst in the Fe^{++}, H_2O_2 reaction,[3] the O_2, $SO_3^=$ reaction,[13] and in the Fe^{++}, O_2 reaction in H_2SO_4,[4] the catalytic role of Cu^{++} in the present system was evaluated. This evaluation was of practical interest to determine whether any of the phenomena described in the previous sections were actually due to Cu^{++} impurity. The effects discovered are rather complex and have been investigated at only one phosphate buffer concentration.

Several features of the copper catalysis are immediately apparent in Fig. 3 which presents the results of a series of runs in which the Cu^{++} concentration was varied while all other concentrations remained constant. There is a saturation in the catalytic effect. The catalytic effect is quite marked for $(Cu^{++}) \sim 10^{-6}$ M but hardly increases with increasing (Cu^{++}) for concentrations greater than 10^{-3} M. Furthermore, for high values of (Cu^{++}), the course of any one reaction is no longer first order, and the values of $-d \ln (Fe^{++})/dt$ decrease as the reaction proceeds. In fact, the rate at high (Cu^{++}) is approximately proportional to $(Fe^{++})^2/(Fe^{+++})$; these features of the rate law have also been demonstrated by initial rate measurements at high Cu^{++} concentrations in independent experiments.

The following mechanism completely accounts for the results

$$Fe^{++} + O_2 \xrightarrow{k_1} Fe^{+++} + HO_2$$

$$Fe^{++} + Cu^{++} \underset{k_8}{\overset{k_7}{\rightleftharpoons}} Fe^{+++} + Cu^{+}$$

$$Cu^{+} + O_2 \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} Cu^{++} + HO_2$$

$$Fe^{++} + HO_2 \xrightarrow{k_3} Fe^{+++} + H_2O_2$$

$$2Fe^{++} + H_2O_2 \longrightarrow 2Fe^{+++} + H_2O \qquad (5)$$

As remarked before, the equations are not balanced with respect to (H^+) and no distinction is intended between the kinetic roles of HO_2 and O_2^-, or of H_2O_2 and HO_2^-. Reaction 5 is, of course, an over-all fast reaction, not a single kinetic step.

Reaction 1 initiates the uncatalyzed reaction. Reaction 7 initiates a catalytic cycle; the resulting Cu^+ ions can either react with oxygen (9) or undergo the back reaction 8. Similarly HO_2 radicals can either be destroyed by reaction with Cu^{++} (10)

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(13) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, Oxford, 1946, p. 234.

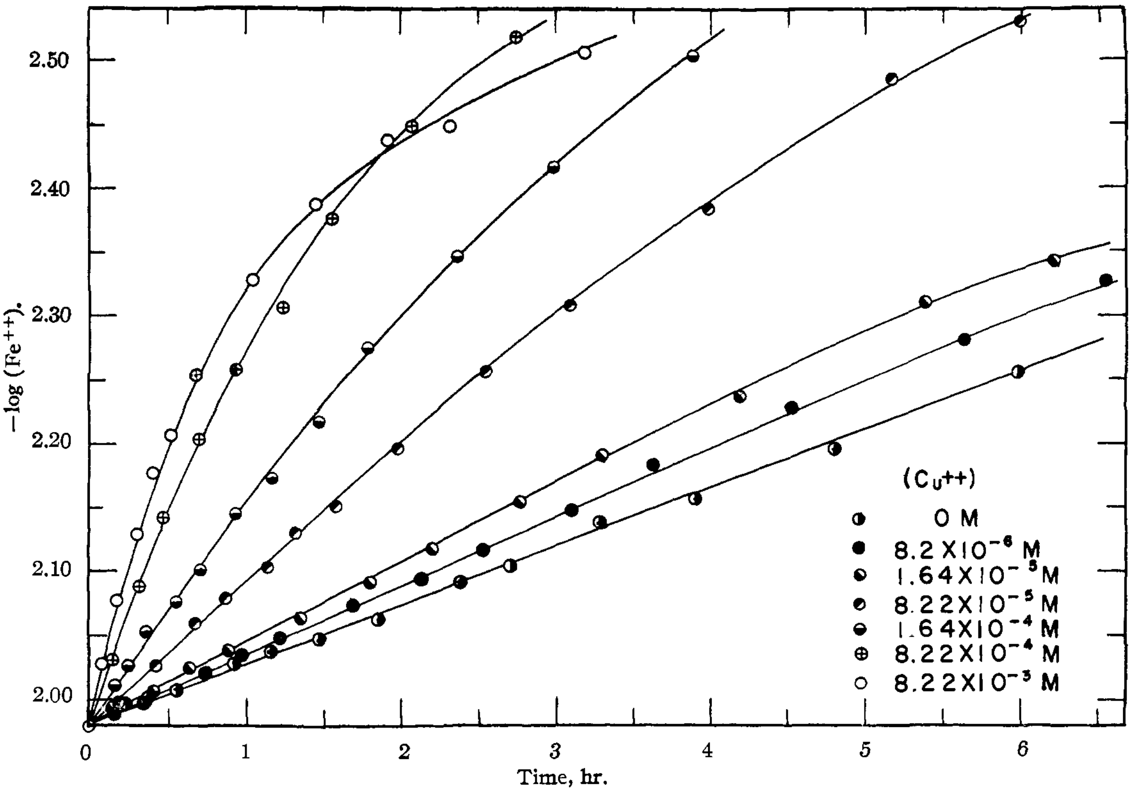

Fig. 3.—Copper catalysis of the $\mathrm{Fe^{II}}$, O_2 reaction: $(\mathrm{Fe}^{++}) = 1.05 \times 10^{-2}$ *M*, $(\mathrm{Fe^{III}}) = 1.02 \times 10^{-2}$ *F*, 30°, $\mu = 1$ *M* $(H_3PO_4) = 0.434$ *F*, $(H_2PO_4^-) = 0.302$ *F*, $p_{O_2} = 150$ mm.

or can react successfully with Fe^{++} (3). Step (10) accounts for the saturation of the catalytic effect as (Cu^{++}) increases. Reaction 8 accounts for the inhibition by Fe^{+++} ions, and allows for the downward curvature of the first-order plots. The results permit the determination of k_7, k_9/k_8 and k_{10}/k_3. It may be noted that one possible simplification in the scheme would occur if $k_9(O_2) << k_8(\mathrm{Fe}^{+++})$, in which case Cu^+ would be in instantaneous equilibrium with Fe^{++}, Cu^{++} and Fe^{+++}. However, it is impossible to fit the data quantitatively with this simplification, and one is led to the complete reaction scheme above. By applying the steady state condition to Cu^+ and HO_2, the rate law that results is

$$-\frac{d(\mathrm{Fe}^{++})}{dt} = 4\,\frac{k_1(\mathrm{Fe}^{++})(O_2)\left[1 + \dfrac{k_9(O_2)}{k_8(\mathrm{Fe}^{+++})}\right] + \dfrac{k_9k_7}{k_8}\,\dfrac{(\mathrm{Fe}^{++})(\mathrm{Cu}^{++})(O_2)}{(\mathrm{Fe}^{+++})}}{1 + \dfrac{k_9(O_2)}{k_8(\mathrm{Fe}^{+++})} + \dfrac{k_{10}(\mathrm{Cu}^{++})}{k_3(\mathrm{Fe}^{++})}}$$

From the observed initial rates, for the experiments of Fig. 3 in which only (Cu^{++}) was varied, and for a series of reactions at low (Cu^{++}) (16×10^{-6} *M*) with varying $(\mathrm{Fe}^{+++})_0$, values of all the pertinent constants were computed by a systematic trial and error process. The calculated values for the initial rates for all these data (first 10 entries in Table VI), agree satisfactorily with the observed rates; the same constants were used to predict satisfactorily the initial rates at high (Cu^{++}) with varying $(\mathrm{Fe}^{+++})_0$ (last three entries in Table VI). The values of the constants used are: $k_1 = 1.33 \times 10^{-1}$ atm.$^{-1}$ hr.$^{-1}$; $(k_9/k_8) = 5.1 \times 10^{-2}$ M^1 atm.$^{-1}$; $(k_{10}/k_3) = 23$; $k_7 = 1.0 \times 10^3$ M^{-1} hr.$^{-1}$.

TABLE VI

CATALYTIC EFFECTS OF Cu^{++}

$t = 30.0°$, $p_{O_2} = 150$ mm., $(H_3PO_4) = 0.434$ *F*, $(H_2PO_4^-) = 0.302$ *F*, $\mu = 1.0$–1.1 *M*, $(R)_0 = -(d(\mathrm{Fe}^{++})/dt)_{t=0}$.

$(\mathrm{Fe}^{++})_0$, *F* $\times 10^2$	$(\mathrm{Fe}^{+++})_0$, *F* $\times 10^2$	(Cu^{++}), *F* $\times 10^6$	$(R_{\mathrm{obsd.}})_0 \times 10^{+2}$	$(R_{\mathrm{calcd}})_0$
1.05	1.02	0	1.10	1.10
1.05	1.02	8.22	1.28	1.26
1.05	1.02	16.4	1.45	1.42
1.05	1.02	82.2	2.69	2.58
1.05	1.02	164	3.94	3.83
1.05	1.02	822	10.2	9.58
1.05	1.02	8220	15.3	17.1
1.05	1.02	16.4	1.38	1.42
1.05	0.51	16.4	1.52	1.54
1.05	0.102	16.4	1.60	1.73
1.00	2.16	8220	10.2	7.57
1.00	1.08	8220	15.9	14.8
1.00	0.216	8220	51.4	62.7

The measurement of the initial rates at high copper concentrations is difficult because they are so great and change rapidly as the reaction proceeds. This is especially true for low initial (Fe^{+++}). This problem was solved by measuring the slope between two points after the reaction had proceeded 10–20%, and extrapolating to zero time by assuming the simplified, approximate rate law, rate $= k(\mathrm{Fe}^{++})^2/(\mathrm{Fe}^{+++})$.

The effect of the initial (Fe^{++}) on the rate is examined in Table VII. The rates are too fast to be measured with great accuracy, but it is clear that at high cupric concentration ($\sim 8 \times 10^{-3}$ *M*) a second-order dependence on (Fe^{++}) is approximately correct and that the detailed numerical predictions of the rate law are confirmed.

TABLE VII

EFFECT OF $(Fe^{++})_0$ AT HIGH (Cu^{++})

$(Cu^{++}) = 0.00822$ *F*, $(Fe^{+++})_0 = 0.0102$ *F*, $(H_2PO_4^-) = 0.302$ *F*, $(H_3PO_4) = 0.434$ *F*, $\mu = 1.0$–1.1 *M*, $p_{O_2} = 150$ mm., $t = 30.0°$.

$(Fe^{++})_0$, *F* $\times 10^2$	*R* mole/l. $\times 10^3$ Obsd.	Calcd.
0.210	0.83	0.745
0.629	7.2	6.38
1.05	14.7	17.1

The success of the kinetic analysis in explaining the course of any one reaction with time is displayed in Table VIII in which observed and theoretical slopes at several points for several representative runs are compared.

TABLE VIII

VARIATION OF RATE WITH DEGREE OF REACTION

$t = 30.0°$, $p_{O_2} = 150$ mm., $(H_3PO_4) = 0.434$ *F*, $(H_2PO_4^-) = 0.302$ *F*, $\mu = 1.0$–1.1 *M* $l = -\text{d} \ln (Fe^{++})/\text{d}t$

$(Fe^{++})_0$, *F* $\times 10^2$	$(Fe^{+++})_0$ *F* $\times 10^2$	(Cu^{++}) $\times 10^6$	*t*, hr.	(Fe^{++}) (obsd. at time *t*) $\times 10^2$	(Fe^{+++}) $\times 10^2$	$l \times 10^3$ Obsd.	Calcd.
1.05	1.02	8.22	0	1.05	1.02	0.256	0.246
			1.00	0.810	1.26	.246	.222
			3.00	0.502	1.57	.223	.189
1.05	1.02	164	0	1.05	1.02	.375	.365
			1.00	0.712	1.36	.362	.294
			2.67	0.413	1.66	.264	.223
1.05	1.02	822	0	1.05	1.02	.971	.912
			0.583	0.678	1.39	.614	.567
			1.00	0.540	1.53	.478	.452

In concluding this section, it is important to note that the dependence on p_{O_2} of the copper-catalyzed rate has not been investigated but in all other respects the proposed rate law has been found to fit the facts. The dependence of the various constants on the phosphate buffer concentrations have not been investigated.

Discussion

We have emphasized previously that there are some unexplained discrepancies as to the dependence of rate on oxygen pressure, but that it appears that, in the absence of Cu^{++}, the oxygenation is a homogeneous reaction, and that the rate law is $-\text{d}(Fe^{++})/\text{d}t = k(Fe^{++})(O_2)(H_2PO_4^-)^2$. At an ionic strength of 1.0 and at 30° the value of *k* is 4.5 (±0.3) atm.$^{-1}$ mole^{-2} liter^2 hr.$^{-1}$.

The first-order dependence of rate on (Fe^{++}) and (O_2) is consistent with the Weiss one-electron HO_2 mechanism. It is also possible that the mechanism involves Fe^{IV} and H_2O_2

$$Fe^{II} + O_2 \longrightarrow Fe^{IV} + H_2O_2$$
$$Fe^{IV} + Fe^{II} \longrightarrow 2Fe^{III}$$
$$2Fe^{II} + H_2O_2 \longrightarrow 2Fe^{III} + 2H_2O$$

No inhibition by iron(III) was observed due to the reaction

$$Fe^{III} + HO_2 \longrightarrow Fe^{II} + O_2 \qquad (2)$$

If the HO_2 mechanism is correct, this is because the reaction in which HO_2 is an oxidizing agent

$$Fe^{II} + HO_2 \longrightarrow Fe^{III} + H_2O_2 \qquad (3)$$

is too fast. The ratio k_2/k_3 at *p*H 2 has been measured as about 0.2 at *p*H 1.7 in the absence of phosphate and at low ionic strength.[3] The complexing of Fe^{III} by phosphate presumably decreases the rate of (2).

The rate law in the presence of copper is more complex and its numerical confirmation strongly supports the proposed mechanism which involves HO_2 as an intermediate. This does not necessarily prove that HO_2 occurs in the uncatalyzed reaction.

From the thermodynamic estimates for HO_2 quoted by Uri,[14] and standard thermodynamic data for the Fe^{++}, Fe^{+++} couple,[15] one computes

$$Fe^{++} + O_2 + H^+ \longrightarrow HO_2 + Fe^{+++},\ \Delta H^0 = 20 \text{ kcal.},\ \Delta F^0 = 28$$

The effect of a phosphate medium would be to make ΔH and ΔF less positive, so that these estimates are consistent with the observed activation energy of 20 kcal. In the study of the effect of Cu^{++} on the Fe^{++}, H_2O_2 reaction, the ratio k_{10}/k_3 for the reactions

$$HO_2 + Cu^{++} \longrightarrow Cu^+ + O_2 \qquad (10)$$
$$HO_2 + Fe^{++} \longrightarrow Fe^{+++} + H_2O_2 \qquad (3)$$

has been estimated as about 7 (±1) at *p*H 1.6 (the ratio is *p*H dependent because of the ionization of HO_2)[3] as compared with the value of 23 measured here. It is not probable that there are strong complexes between phosphate and Cu^{++} or Fe^{++} so that the ratio k_{10}/k_3 should not be greatly different in the two experiments. The half-order of magnitude agreement between the two numbers is satisfying.

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[14] N. Uri, *Chem. Revs.*, **50**, 309 (1952).

[15] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1952, p. 261.