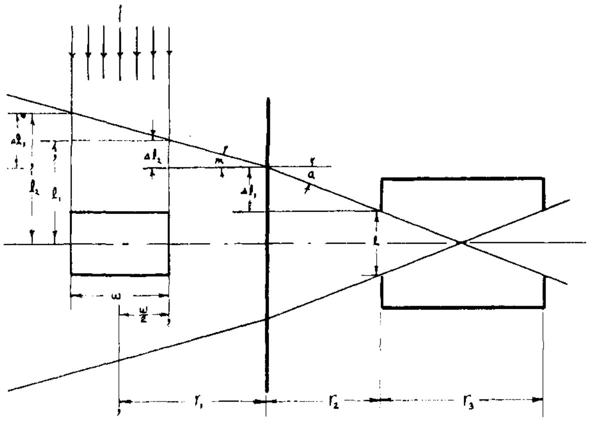

Fig. 5.—Diagram of optical system used in derivation of expression for C_V.

may be due to the common ion effect. The lower pH favors the formation of more undissociated acid and the system thus approaches the conditions for which the light scattering treatment is valid.

For the 9-phosphotungstic acid, the pH has no effect, the turbidity in pure water and at pH of 2 being identical. This probably is due to the fact that the 9-phosphotungstic acid is so strong that the additional hydronium ion does not produce sufficient undissociated acid to affect the turbidity.

In order to relate the light scattering of a non-ideal substance to the molecular weight, it is necessary to revert to equation 2. By utilizing the Gibbs–Duhem relation

$$N_1 \, d \ln f_1 + N_2 \, d \ln f_2 = 0 \qquad (5)$$

where N_1 and N_2 are mole fractions, it can be shown that in dilute solutions

$$\tau_e = \frac{HM_2}{d \ln f_2/dc} = \frac{HM_2}{d \ln a_2/dc} \qquad (6)$$

Thus the determination of the molecular weight requires in addition to the turbidity, knowledge of d ln a_2/dc. This relation is perfectly general in moderately dilute solutions.

We are now engaged in determining d ln a_2/dc for 12- and 9-phosphotungstic acids from measurements of cells with transference, transference number and dissociation constants. We will report on this work in a subsequent communication.

Appendix

The correction factor C_V' which is the volume seen by the photomultiplier tube in non-aqueous solvents compared to that in water may be derived with the aid of Figs. 1 and 5.

$$R_V = \frac{l^2 w}{(l_1 + l_2)^2 w} = \frac{l^2}{(l_1 + l_2)^2} \qquad (7)$$

where R_V = ratio of volume l^2w to the actual volume seen by the photomultiplier tube in the presence of a liquid with refractive index n. When the angle m is sufficiently small so that sin $m \cong$ tan m, it can be shown that

$$l_1 = l\left(\frac{1}{2} + \frac{r_2}{r_3} + \frac{r_1 - w/2}{n\sqrt{l^2 + r_3^2}}\right) \qquad (8)$$

and

$$l_2 = l\left(\frac{1}{2} + \frac{r_2}{r_3} + \frac{r_1 + w/2}{n\sqrt{l^2 + r_3^2}}\right) \qquad (9)$$

It follows that

$$R_V = \left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n\sqrt{1^2 + r_3^2}}\right)^{-2} \qquad (10)$$

The light radiated by the excess volume is only half as intense as that radiated by the volume l^2w.[11] The ratio of the light scattered by the volume l^2w to the total volume seen by the photomultiplier tube is

$$C_V = 2\left[\left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n\sqrt{l^2 + r_3^2}}\right) + 1\right]^{-1} \qquad (11)$$

and the correction factor for non-aqueous solvents becomes

$$C_V' = \frac{\left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n_w\sqrt{1 + r_3^2}}\right)^2 + 1}{\left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n\sqrt{l^2 + r_3^2}}\right)^2 + 1} \qquad (12)$$

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[11] C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950).

POTSDAM, N. Y.

[CONTRIBUTION NO. 2260 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Kinetics of the Ferrous Iron–Oxygen Reaction in Acidic Phosphate–Pyrophosphate Solutions

BY JAMES KING AND NORMAN DAVIDSON[1]

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The rate law for the ferrous iron–oxygen reaction in acid solutions (pH ~1–2) containing phosphate and pyrophosphate anions is $-$ d(Fe^{++})/dt = k_1(Fe^{++})(H$_2$PO$_4^-$)^2P_{O_2} + k_2(Fe^{++})(H$_2$P$_2$O$_7^=$)P_{O_2} where k_1 = 1.08(±0.06) × 10^{-3} atm.$^{-1}$ mole^{-2} liter^2 sec.$^{-1}$ and k_2 = 2.13(±0.05) × 10^{-2} atm.$^{-1}$ mole^{-1} liter sec.$^{-1}$ at 30° (μ = 1.0–1.1 mole/liter, NaClO$_4$). The activation energies are $\Delta H_1^* = 21(\pm 1)$ and $\Delta H_2^* = 6(\pm 1)$ kcal. The rate law and the values of k_1 and k_2 both show that $H_2P_2O_7^=$ and $H_2PO_4^-$ are independent catalysts and that the unusual quadratic dependence on ($H_2PO_4^-$) is not due to the equilibrium $2H_2PO_4^- \rightleftarrows H_2P_2O_7^= + H_2O$. The mechanism of the reaction presumably involves as the rate-determining step either the one electron transfer process $Fe^{II} + O_2 \rightarrow Fe^{III} + O_2^-$ or the two-electron process $Fe^{II} + O_2 \rightarrow Fe^{IV} + O_2^=$, with iron in the transition state stabilized by the complexing phosphorous anions.

Cher and Davidson[2] found that the rate law for the oxygenation of Fe^{II} in phosphoric acid solution is $-$d(Fe^{++})/dt = k_1(Fe^{++})P_{O_2}(H$_2$PO$_4^-$)^2. The quadratic dependence on (H$_2$PO$_4^-$) is somewhat

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[1] We are indebted to the Atomic Energy Commission for support of this research under Contract AT(11-1)-188; and to the Danforth Foundation and the General Education Board for fellowships to one of us (J.K.). This paper was presented in part at the 129th National Meeting of the A. C. S., Dallas, April, 1956.

[2] M. Cher and N. Davidson, THIS JOURNAL, **77**, 793 (1955).

unusual. A linear dependence would be expected in view of: (a) general experience with this kind of reaction; (b) the reported first-order dependence on (F^-) for the fluoride catalysis of the Fe^{II}, O_2 reaction[3]; and (c) the reported fact that the first complex formed between Fe^{+++} and phosphate anions in acid solution contains one phosphate per iron, being either $FeHPO_4^+$ or $FeH_2PO_4^{++}$.[4,5] The quadratic dependence on dihydrogen phosphate concentration would be explained if the actual catalyst were dihydrogen pyrophosphate, formed in equilibrium amounts according to the reaction

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

This hypothesis and a general interest in the effects of pyrophosphate stimulated the present work.

Spoehr[6] and Smith and Spoehr[7] have reported that there is an accelerating influence of pyrophosphate on the Fe^{II}–O_2 reaction. The latter authors claim that the rate law is $-d(Fe^{II})/dt = k(Fe^{II})(O_2)$; but a later study[8] of the effects of stirring indicates that the reaction rate was diffusion controlled under the conditions employed.

Other references to studies of the Fe^{II}–O_2 reaction in various media are given in another paper from this Laboratory.[9]

Experimental

The rate of O_2 uptake was measured by a manometric method with a Warburg apparatus, as described previously.[2] The apparatus was well thermostated and had provisions for vigorous shaking of the reaction mixtures.

Reagent grade ferrous ammonium sulfate and sodium hydroxide were used. Sodium perchlorate, for maintaining ionic strength, was prepared by neutralization of known amounts of 85% perchloric acid with sodium hydroxide. The commercial redistilled water used in the initial experiments was found to contain trace amounts of copper. For all the results reported here, water was prepared by redistilling the commercial distilled water in a Pyrex, electrically heated still, to remove the traces of copper. The necessary precautions were taken to exclude dust from the vessels and each reaction vessel was pre-rinsed with the redistilled water. The desired H_3PO_4–$H_2PO_4^-$ buffer solutions were prepared by the appropriate neutralization of reagent grade phosphoric acid with standard sodium hydroxide solution. Pyrophosphate solutions were prepared from weighed quantities of reagent grade $Na_4P_2O_7 \cdot 10H_2O$ and checked acidimetrically.

The procedure was to dissolve separately ferrous ammonium sulfate and sodium pyrophosphate in phosphate buffer. Corrections of the H_3PO_4–$H_2PO_4^-$ ratio were made for the effects due to the conversion of $P_2O_7^{-4}$ to $H_2P_2O_7^{-2}$ and $H_3P_2O_7^{-1}$. Varying amounts of the two solutions were placed in the 15-ml. reaction flasks, the total volume of solution always being 5 ml. The flasks were then quickly attached to the manometric apparatus and the shaking mechanism started. 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 was bubbled through water, filtered through glass wool, passed into the system through the stopcock at the top of the manometer and out through an outlet on the side of the reaction flask. Approximately 1/2 liter of gas was passed through the system in about five minutes.

The time lapse between preparation of the samples and actual observation of the change in oxygen pressure introduced an error not greater than 3%. This was checked by determining the Fe^{++} concentration by permanganate titration in such a solution three minutes after mixing.

All the glass joints were lubricated with Apiezon grease (M). Excess grease added to the reaction vessel did not affect the rate. It has been shown[2] previously that the reactions taking place in the Warburg reaction flasks are not diffusion controlled.

Results

Effect of Fe^{II} and Fe^{III} Concentrations.—The rate of oxidation is first order in ferrous iron concentration. This is evident from a study of the variation of initial rate with initial (Fe^{II}) at fixed phosphate and pyrophosphate concentration (Table I). Throughout this paper, M and F stand for mole liter^{-1} and formula wt. liter^{-1}, respectively. The molar concentrations of H_3PO_4, $H_2PO_4^-$, $H_3P_2O_7^-$ and $H_2P_2O_7^=$ in Table I are calculated assuming acid constants of 0.020 and 0.021 M for H_3PO_4 and $H_3P_2O_7^-$, respectively.

TABLE I

EFFECT OF Fe^{II} ON INITIAL REACTION RATE

$m = -d \ln(Fe^{II})/dt$ (hr.$^{-1}$), $(H^+) = 0.0177$ M, $(H_3PO_4) = 0.188$ M, $(H_2PO_4^-) = 0.212$ M, $(H_3P_2O_7^-) = 0.0023$ M, $(H_2P_2O_7^=) = 0.0027$ M, μ (ionic strength) = 1.0 – 1.1 M ($NaClO_4$), $P_{O_2} = 151$ mm., $T = 30°$

$(Fe^{II})_0$ (F)	0.003	0.010	0.020
m (hr.$^{-1}$)	.0789	.0772	.0800

It was not practicable to vary the Fe^{II} concentration over a larger range than that displayed in Table I. With lower concentrations, the manometer change due to reaction is small compared to fluctuations in the control (no Fe^{II}) runs. With higher concentrations, the reaction is too fast.

When $-\ln(Fe^{II})$ is plotted against t, fairly good straight lines (*cf.*, Fig. 1 of ref. 2) are obtained. At about 60% reaction, there was a decrease in slope of 10–20%. Usually at about 70% reaction, a white precipitate, believed to be ferric pyrophosphate, slowly formed. Addition of ferric ion initially produced the same phenomena immediately. Therefore, a detailed study of the kinetic effects of Fe^{III} addition did not appear to be profitable. Values for rate constants were taken from lines drawn through points up to about 40% reaction.

Effect of Phosphate Concentration.—In agreement with Cher and Davidson, we find that $-d \ln(Fe^{II})/dt = k_1(H_2PO_4^-)^2 P_{O_2}$. These results are given in Table II.

TABLE II

PHOSPHATE CATALYSIS OF THE Fe^{II}–O_2 REACTION

(30°, $\mu = 1.0 - 1.1$ M, $NaClO_4$)

$(Fe^{II})_0$, M	(H_3PO_4), M	$(H_2PO_4^-)$, M	P_{O_2}, atm.	k_1, atm.$^{-1}$ M^{-2} hr.$^{-1}$
0.0100	0.200	0.200	0.198	4.00
.0100	.200	.200	.942	3.95
.0100	.415	.389	.198	3.96
.0100	.415	.389	.942	3.78
.0050	.415	.389	.198	3.64
.0050	.415	.389	.942	3.56
.010	.800	.200	.198	4.43

Av. k_1 = 3.90 (±0.22, mean error)

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

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

[5] T. Yamane and N. Davidson, unpublished work in this Laboratory.

[6] H. A. Spoehr, THIS JOURNAL, **46**, 1494 (1924).

[7] J. H. C. Smith and H. A. Spoehr, *ibid.*, **48**, 107 (1926).

[8] A. B. Lamb and L. W. Elder, *ibid.*, **53**, 137 (1931).

[9] R. E. Huffman and N. Davidson, *ibid.*, **78**, 4836 (1956).

The values of k_1 in Table II are generally somewhat lower (10–20%) than those reported by Cher and Davidson[2]; furthermore the ratio of rates in oxygen and air was close to the theoretical value of 4.8, whereas Cher and Davidson observed about 4.0. These differences probably are due partly to the use of redistilled water containing no Cu^{++} impurity in the present work, although it seems unlikely that this is the entire reason for the numerical discrepancy. The other causes however are unknown.

Effect of Pyrophosphate Concentration.—Pyrophosphate is an effective catalyst for the Fe^{II}-O_2 reaction. This is evident, for example, by noting that the rates recorded in Table I are about 5 times faster than predicted for phosphate catalysis alone.

Yost and Russell[10] quote values for the ionization constants of pyrophosphoric acid at 18° as follows: $K_1 = 0.14$, $K_2 = 0.011$, $K_3 = 2.1 \times 10^{-7}$, $K_4 = 4.06 \times 10^{-10}$; in 1 *M* KCl, $K_2 = 0.027$, $K_3 = 3 \times 10^{-6}$. The species present in significant amounts with $0.01 < (H^+) < 0.07$ are $H_3P_2O_7^-$ and $H_2P_2O_7^=$; it is accordingly necessary to determine a value of K_2 under the conditions of our experiments. This was done using a *p*H meter to measure the hydrogen ion concentration of solutions containing varying amounts of $H_3P_2O_7^-$ and $H_2P_2O_7^=$ at $\mu = 1.0$ ($NaClO_4$). A NaCl salt bridge was used because of the insolubility of $KClO_4$. The *p*H meter was calibrated to read 2.09 for 0.00814 *M* HCl in 1.00 *M* $NaClO_4$ at 30°. The results are shown in Table III. We have used $K_2 = 0.021$ *M* for the concentration ionization quotient of $H_3P_2O_7^-$ in interpreting the kinetic results (*cf.*, the discussion in footnote 13).

TABLE III

MEASUREMENT OF THE SECOND IONIZATION QUOTIENT OF PYROPHOSPHORIC ACID

($T = 30°$, $\mu = 1.0$ *M*, solutions prepared from standard HCl and $Na_4P_2O_7$ solutions.)

(H^+), *M*	$(H_3P_2O_7^-)$, *M*	$(H_2P_2O_7^=)$, *M*	K_2, *M*
0.00955	0.00874	0.00218	0.0239
.00912	.00918	.00213	.0212
.0126	.0118	.00187	.0200
.0120	.0124	.00180	.0176

The results of a set of runs in which $(H_2PO_4^-)$, $(H_3P_2O_7^-)$ and $(H_2P_2O_7^=)$ are all varied independently are exhibited in Table IV. These results show that the phosphate and pyrophosphate catalysis are independent and additive; and that the pyrophosphate catalysis is due principally to, and is first order in $H_2P_2O_7^=$; *i.e.*, that the rate law is $-d\ln(Fe^{II})/dt = k_1' (H_2PO_4^-)^2 + k_2' (H_2P_2O_7^=)$ (in air, 30°). This result is demonstrated by the constancy of the calculated values of k_2', taking $k_1' = 0.794\ M^{-2}\ hr.^{-1}$, with $(H_2PO_4^-)$ varied by a factor of 2, $(H_2P_2O_7^=)$ varied by a factor of 5.7, and $(H_3P_2O_7^-)/(H_2P_2O_7^=)$ varied by a factor of 3.8, all independently.

Unfortunately, a thoroughly satisfactory study of the effect of O_2 pressure on the pyrophosphate reaction path was not carried out. One series of runs was made at a time when difficulty with nonreproducible results was being encountered. This series gave ratios of rates in oxygen to rates in air of 3.7–4.3. The air results showed more scatter than the oxygen results. Comparison of the most consistent oxygen results obtained at this time with the consistent air results (Table IV) obtained later gives a ratio of 4.7 (±0.2). On this basis, it seems to us to be clear that the rate of the pyrophosphate catalyzed reaction is essentially proportional to the oxygen pressure and we write

$$-d\ln(Fe^{++})/dt = k_1(H_2PO_4^-)^2P_{O_2} + k_2(H_2P_2O_7^=)P_{O_2}$$

TABLE IV

RATES IN THE PRESENCE OF PYROPHOSPHATE

$(Fe^{II})_0 = 0.010$ *M*, $T = 30°$, $\mu = 1.0$–1.1 *M* ($NaClO_4$)
$P_{O_2} = 151$ mm., $k'_1 = 0.793\ M^{-2}\ hr.^{-1}$

(H^+), *M*	(H_3PO_4), *M*	$(H_2PO_4^-)$, *M*	$(H_3P_2O_7^-)$, *M*	$(H_2P_2O_7^=)$, *M*	k'_2, M^{-1} hr.$^{-1}$
0.0650	0.765	0.235	0.00945	0.00305	15.00
.0546	.732	.268	.01800	.00730	15.91
.0402	.667	.333	.03280	.01720	15.68
.0176	.188	.212	.00225	.00272	15.05
.0176	.377	.427	.00602	.00698	15.10
.0173	.373	.431	.00770	.00930	15.58
.0169	.369	.435	.00850	.01050	14.69
.0157	.176	.224	.00424	.00576	15.29

Av. $k_2' = 15.29$ (±0.33, mean error)

Effect of Surface.—Rate measurements in which Pyrex glass wool was added to the reaction flasks were performed in order to investigate possible surface catalytic effects. The surface area of the glass fibers[2] is estimated as 2300 cm.^{2} g.$^{-1}$. The surface area of the reaction flasks is about 50 cm.^{2}. Before introduction into the reaction flasks, the glass wool was heated to 500° in an oven for an hour, washed with hot aqua regia, rinsed copiously with water, dried and transferred to the cells. The results, presented in Table V, indicate that there is a negligible amount of surface reaction.

TABLE V

THE EFFECT OF SURFACE ON REACTION RATE

$m = -d\ln(Fe^{++})/dt$ (hr.$^{-1}$), $\mu = 1.01$–1.1 *M* ($NaClO_4$),
$T = 30°$, $P_{O_2} = 151$ mm.

(Fe^{++}), *M*	(H^+), *M*	$(H_2PO_4^-)$, *M*	$(H_2P_2O_7^=)$, *M*	Surface area, cm.^{2}	*m*, hr.$^{-1}$
0.020	0.020	0.200	0	50	0.0396
.020	.020	.200	0	985	.0264
.020	.0181	.210	0.00215	50	.0625
.020	.0181	.210	.00215	726	.0534
.020	.0165	.219	.00448	50	.1025
.020	.0165	.219	.00448	1007	.1040
.010	.0143	.234	.0083	50	.179
.010	.0143	.234	.0083	650	.200

Effect of Temperature.—A set of runs was performed at 20° in air at $(H^+) = 0.017$–0.024, with variable amounts of pyrophosphate. These results gave k_1' (air, 20°) $= 0.25$ (± 0.01) M^{-2} hr.$^{-1}$ and k_2' (air, 20°) $= 10.70$ (±1.0) M^{-1} hr.$^{-1}$. For this calculation, it is assumed that the ionization constant of $H_3P_2O_7^-$ does not change very much between 20 and 30°. It is known that K_1 and K_2 for H_3PO_4 do not change very much. The activation energies for the phosphate and pyrophosphate paths are calculated to be 21 (±1) and 6 (±1)

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[10] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 228.

kcal. mole^{-1}. Cher and Davidson gave 20 (±2) for the former.

Discussion

We may summarize the results of the experiments with the rate law

$$-\,d\ln(\mathrm{Fe}^{++})/dt = k_1(\mathrm{H_2PO_4^-})^2 P_{\mathrm{O_2}} + k_2(\mathrm{H_2P_2O_7^=}) P_{\mathrm{O_2}} \quad \text{(a)}$$

with $k_1 = 3.90$ (±0.22 mean) atm.$^{-1}$ M^{-2} hr.$^{-1}$ (or $k_1 = 1.08\ (\pm 0.06) \times 10^{-3}$ atm. M^{-2} sec.$^{-1}$) and $k_2 = 76.8$ (±1.66) atm.$^{-1}$ M^{-1} hr.$^{-1}$ (or $k_2 = 2.13\ (\pm 0.05) \times 10^{-2}$ atm.$^{-1}$ M^{-1} sec.$^{-1}$) at 30° and activation energies of 21 (±1) and 6 (±1) kcal., respectively. Of course, the result does not mean that $H_3P_2O_7^-$ is not a catalyst; but the data indicate that it is less than, say, 10% as effective as $H_2P_2O_7^=$. Correspondingly, it is quite possible that catalytic effects due to $HP_2O_7^{\equiv}$ would be significant at higher *p*H's where the concentration of this ion is larger.

The results show that the quadratic dependence on ($H_2PO_4^-$) is not due to the equilibrium

$$2\mathrm{H_2PO_4^-} \rightleftharpoons \mathrm{H_2P_2O_7^=} + \mathrm{H_2O} \qquad \text{(b)}$$

$$\frac{(\mathrm{H_2P_2O_7^=})}{(\mathrm{H_2PO_4^-})^2} = K_\mathrm{b}$$

If such were the case, $K_\mathrm{b} = k_1/k_2 = 0.051\ M^{-1}$. We shall now show that available thermodynamic data and reasonable estimates give $K_\mathrm{b} = 6.8 \times 10^{-6}\ M^{-1}$ (with an uncertainty of a factor of perhaps 10–100). Therefore, the observed value of k_1/k_2 is too large by a factor of about 10^4.

For the reaction

$$\mathrm{H_2PO_4^-} + \mathrm{HPO_4^=} \longrightarrow \mathrm{HP_2O_7^{\equiv}} + \mathrm{H_2O} \qquad \text{(c)}$$

$\Delta H = 5810$ (± 130) cal. mole^{-1} [11] (in solutions with $\mu \sim 0.4\ M$ at 25°). From the empirical formula of Connick and Powell,[12] we estimate the entropy of $HP_2O_7^{\equiv}$ as −5.4 e.u. and therefore, for reaction c, $\Delta S = -1.4$ (± 4, estimated) e.u. Therefore ΔF^0 (reaction c, 30°) = 6235 (± 1200), $K_\mathrm{c} = 3.4 \times 10^{-5}\ M^{-1}$, uncertain by a factor of 7.5. The thermodynamic ionization constant of $H_2PO_4^-$ is 6.4×10^{-8}; at $\mu = 1$, we take $2 \times 10^{-7}\ M$. For the ionization constant of $H_2P_2O_7^=$ at $\mu = 1$ we take 1.0×10^{-6}.[13]

Therefore

$$\begin{array}{lll}
\mathrm{H_2PO_4^-} + \mathrm{HPO_4^=} = \mathrm{HP_2O_7^{\equiv}} + \mathrm{H_2O} & 3.4 \times 10^{-5} & \text{(c)} \\
\quad \mathrm{H_2PO_4^-} = \mathrm{HPO_4^-} + \mathrm{H^+} & 2 \quad \times 10^{-7} & \\
\quad \mathrm{H^+} + \mathrm{HP_2O_7^{\equiv}} = \mathrm{H_2P_2O_7^=} & 1.0 \times 10^{6} &
\end{array}$$

and adding, we get

$$\begin{array}{lll}
2\mathrm{H_2PO_4^=} = \mathrm{H_2P_2O_7^=} + \mathrm{H_2O} & 6.8 \times 10^{-6} & \text{(b)}
\end{array}$$

It is very unlikely that this estimate is wrong by a factor of more than 10^2. It therefore is highly probable that k_1/k_2 does not equal K_b, *i.e.*, that the calculated ratio between them of 7.5×10^3 is not all due to experimental error and errors in estimates.

There are other arguments that discredit the hypothesis that the catalytic effect of phosphate is due to pyrophosphate maintained at equilibrium by reaction b. The hydrolysis of pyrophosphate is known to be too slow to maintain such an equilibrium,[14] but it can be imagined that there would be a catalytic effect of iron ions for reactions b. However, if such an equilibrium were maintained, the pyrophosphate added in our experiments would have hydrolyzed rapidly and almost completely, thereby increasing the phosphate concentration slightly and having an imperceptible effect on the rates.

The mechanism of the Fe^{II}–O_2 reaction for the case that the rate is first order in Fe^{II} and first order in O_2 has been discussed frequently before.[2,3,9] The two most attractive possibilities may be written schematically as

$$\mathrm{Fe^{II}} + \mathrm{O_2} \rightleftharpoons \mathrm{Fe^{III}} + \mathrm{HO_2} \qquad (1,2)$$

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

$$\mathrm{Fe^{II}} + \mathrm{H_2O_2} \longrightarrow \text{further oxidation (fast)} \qquad (4)$$

or

$$\mathrm{Fe^{II}} + \mathrm{O_2} \rightleftharpoons \mathrm{Fe^{IV}} + \mathrm{H_2O_2} \qquad (5,6)$$

$$\mathrm{Fe^{II}} + \mathrm{H_2O_2} \longrightarrow \text{further oxidation} \qquad (4)$$

There is at present no compelling reason for favoring one path or the other. The occurrence of the first scheme would be proved by observing inhibition by Fe^{III}, corresponding to competition between reactions 2 and 3. In the present case it was not practicable to search for such an effect because of the formation of complex ions and insoluble solids containing Fe^{III} and pyrophosphate.

Pyrophosphate is a good complexing agent for Fe^{III} and undoubtedly also for Fe^{IV}. Its catalytic effectiveness probably is due to the stabilization of the transition state for reaction 1 or reaction 5 by complexing the iron ion in the transition state molecule, as suggested by Weiss. As pointed out previously,[9] there is a correlation between the complexing affinity of an anion X^- for Fe^{III} and its catalytic effectiveness in the bimolecular Fe^{II}–O_2 reaction.

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[11] J. M. Sturtevant and N. S. Ging, THIS JOURNAL, **76**, 2087 (1954).

[12] R. E. Connick and R. E. Powell, *J. Chem. Phys.*, **21**, 2206 (1953). We are indebted to Professors Connick and Powell for correspondence concerning this matter.

[13] S. M. Lambert and J. I. Watters, THIS JOURNAL, **79**, 4262 (1957), give 7.6×10^{-7} for the quantity $[H^+](HP_2O_7^{\equiv})/(H_2P_2O_7^=)$ at $\mu = 1((CH_3)_4NCl)$ at 25°, where brackets and parentheses indicate activities and concentrations, respectively. We estimate $\gamma_\mathrm{H} = 0.76$, so that the concentration equilibrium constant is $1.0 \times 10^{-6}\ M$. These authors give $[H^+](H_2P_2O_7^=)/(H_3P_2O_7^-) = 6.0 \times 10^{-3}$ at $\mu = 0.1$ at 25°, from which we estimate $K_2 = 8 \times 10^{-3}\ M$ at $\mu = 0.1$ and 25°. This is to be compared with the value 0.021 M at $\mu = 1.0$ and 30° which we have used (*cf.* Table III).

[14] D. O. Campbell and M. L. Kilpatrick, *ibid.*, **76**, 893 (1954).