If reaction (1) is followed by the two steps

$$CH_2 + CH_2CO = CO + (C_2H_4 \text{ or polymer}) \tag{8}$$

$$CH_2 + C_2H_4 = C_3H_6 \tag{20}$$

then

$$\Phi_{CO} = 1 + \frac{k_8(K)}{k_8(K) + k_{20}(E)} \tag{21}$$

where (E) is the ethylene concentration. At 27° k_{20}/k_8 is approximately unity[13] as shown in Table V since $\Phi_{CO} \sim 1.5$ when (K) = (E). k_{20}/k_8 decreases as the temperature increases and $E_8 - E_{20}$ is approximately 4.8 kcal.

In mixtures of ketene, ethylene and oxygen one may assume first that CH_2 does not react with oxygen. If this is true, it will react equally with ketene and with ethylene at 27° if the concentrations of these two gases are equal. In the second run, Table V, the ethylene to ketene ratio is 18.5 so that virtually no CH_2's would react with ketene. Thus, unless CH_2 reacts with ethylene to give an intermediate which reacts with oxygen, there should be no oxygen uptake. This is contrary to the facts. The evidence that a diradical, such as $CH_2CH_2CH_2$, would rearrange to propylene before it would react with oxygen is fairly good but not absolutely exclusive.[18]

If reference is again made to Table V, one finds that the carbon monoxide yields in the first two runs are below two. Since (1) and (11) together would give at least $\Phi_{CO} = 2$, one must assume that the radical CH_2O_2 reacts with ethylene without giving carbon monoxide.

It is difficult to estimate the activation energy difference $E_8 - E_9$ since it must be based on the effect of low oxygen pressures in decreasing the ethylene yield. Very roughly $E_8 - E_9$ is 3 kcal., but the uncertainty is at least 2 kcal. From the data in Table I, k_9/k_8 is about 0.3×10^5 at 27°. If the rate of (8) at 27° is 10^{-16} ml. molecules^{-1} sec.$^{-1}$ [13] then (9) has a rate of about 3×10^{-12} in the same units. If the activation energy is zero, the steric factor P_9 is about 10^{-2} which is somewhat higher than $CH_3 + O_2$[19,20] and possibly higher than $C_2H_5 + O_2$.[21] On the other hand, 9 may have an activation energy as great as 2 kcal., and therefore the steric factor for (9) could be close to unity.

Thus the assumption that methylene radicals react with oxygen much more rapidly than they do with ketene fits the facts on the whole much better than the opposite assumption. Moreover, the results which follow from this assumption tend to show that CH_2 behaves as a true radical and not as a relatively unreactive quasi-molecule.

ROCHESTER, NEW YORK

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Kinetics of the Ferrous Iron–Oxygen Reaction in Sulfuric Acid Solution

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The reaction $4Fe^{II} + O_2 \rightarrow 4Fe^{III} + 2H_2O$, at 140–180° in 1 *F* H_2SO_4, proceeds by simultaneous bimolecular and termolecular reaction paths: $-d(Fe^{II})/dt = k_b(Fe^{II})P_{O_2} + k_t(Fe^{II})^2P_{O_2}$. At 159°, $k_b = 1.93 \times 10^{-5}$ atm.$^{-1}$ sec.$^{-1}$, $k_t = 1.60 \times 10^{-3}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$; the respective activation energies were measured as 13.4 (±2) and 16.3 (±2) kcal. At 30.5°, only the termolecular path is observed (contrary to the predictions of the high temperature activation energies); $k_t = 2.78 \times 10^{-6}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$ (1 *F* H_2SO_4). The variation of rate with $SO_4^=$ ($\mu \sim 1$, $NaClO_4$) indicates independent reactions, $2Fe^{++} + O_2 \xrightarrow{(1/2)k_u} 2Fe^{III} + H_2O_2$, and $FeSO_4 + Fe^{++} + O_2 \xrightarrow{(1/2)k_s} 2Fe^{III} + H_2O_2$, where $k_u = 1.4 \times 10^{-6}$ $k_s = 3.1 \times 10^{-5}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$, and $K_{FeSO_4} = 1.1$ M^{-1}. The reaction rate increases a small amount with increasing *p*H. Catalysis by Cu^{++} follows the rate law $-d(Fe^{++})/dt = 4k_9(Fe^{II})(Cu^{++})$ and is probably initiated by $Fe^{II} + Cu^{++} \xrightarrow{k_9} Fe^{III} + Cu^{I}$. In 0.23 *F* H_2SO_4, 0.35 *F* Na_2SO_4, $k_9 = 1.9 \times 10^{-3}$ M^{-1} sec.$^{-1}$. The rate-determining step for the bimolecular path is presumably either: (1a) $Fe^{II} + O_2 \rightarrow Fe^{III} + HO_2$, or (1b) $Fe^{II} + O_2 \rightarrow Fe^{IV} + H_2O_2$; for the termolecular path it is $2Fe^{II} + O_2 \rightarrow 2Fe^{III} + H_2O_2$. Possible detailed mechanisms are discussed. There is evidence that the bimolecular path, the termolecular path and the Cu^{++} catalyzed path are all accelerated by complexing anions, X, and to an extent depending on the affinity of X for Fe^{+++}. Furthermore, strong complexers favor the occurrence of the bimolecular path.

The rate of oxidation of ferrous ion by molecular oxygen in acid solution is very dependent upon the nature of the anions present. The rate increases as the complexing affinity of the anion for ferric ion increases. (It is to be expected that the complexing affinity for ferrous ion would be in the same order.) Thus, at a given *p*H, the rate is found to decrease in the series pyrophosphate,[2] phosphate,[3] chloride,[4,5] sulfate[6] and perchlorate.[7] The rate law is $-d(Fe^{II})/dt = 4k(Fe^{II})P_{O_2}$ for the first three media listed above and $-d(Fe^{II})/dt = 4k(Fe^{II})^2 \cdot P_{O_2}$ for the last two. The rate-determining steps are believed to be either (1a) or (1b) for the former case, and (2) for the latter.

$$Fe^{II} + O_2 \longrightarrow Fe^{III} + HO_2 \tag{1a}$$

$$Fe^{II} + O_2 \longrightarrow Fe^{IV} + H_2O_2 \tag{1b}$$

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

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Reaction (1a) is the first step in the Weiss one-electron oxidation mechanism.[8,9] The reactions as written are not balanced with respect to hydrogen ion; they are intended to indicate the oxidation changes involved but not to specify the dependence of rate upon acidity. The symbol $(\mathrm{Fe^{II}})$ is defined as the formal concentration of ferrous iron; $(\mathrm{Fe^{++}})$ means the concentration of the uncomplexed ion. A similar convention is used for other atomic species.

It was thought that the bimolecular reaction (1a or 1b), which involves one of the unstable intermediates, HO_2 or $\mathrm{Fe^{IV}}$, would have a higher activation energy than the termolecular path (2) and would be more important at high temperatures. We have accordingly studied the ferrous iron, oxygen reaction at 140–180° in sulfuric acid. These results prompted a further investigation of the reaction in various solutions of sulfuric acid and sodium sulfate at room temperature and at ferrous iron concentrations considerably lower than those used by previous investigators. Some information on the cupric ion catalyzed reaction was also obtained.

Experimental

The experimental techniques for the high and low temperature reactions were different and will be described separately. The amount of ferric ion produced at given times was determined in both cases by measuring the ultraviolet absorption of the ferric sulfate complex ion[10] with a Beckman DU spectrophotometer.

Reagent grade ferrous ammonium sulfate, ferric ammonium sulfate, cupric sulfate and sodium sulfate were used. Sulfuric and perchloric acid solutions were prepared from concentrated reagent grade acids. Sodium perchlorate was prepared by neutralizing sodium hydroxide solutions with perchloric acid. The water used for high temperature reactions was prepared by redistilling tap distilled water from alkaline permanganate solution in a Pyrex, electrically heated still. The commercial redistilled water used in the first low temperature studies was found to contain trace amounts of copper. The water used in all results reported here at room temperature was prepared by redistilling the commercial distilled water in a Pyrex, electrically heated still to remove these traces of copper. In all cases, precautions were taken to exclude dust and to rinse vessels with the pure distilled water before preparing solutions. Tank oxygen was bubbled through water and filtered through glass wool before use.

A high temperature reaction cell consisted of an 8 cm. length of 15 mm. Pyrex tubing and, as a neck, an 11 cm. length of 5 mm. tubing. About 5 ml. of reaction solution was added, and air was displaced by a stream of O_2 gas introduced through a narrow capillary. The neck was then quickly sealed off in the middle while a stream of O_2 was still passing through the top of the neck.

The sealed reaction tubes were wrapped in glass wool and placed in short sections of iron pipe closed with pipe caps. The high temperatures were provided by a silicone oil-bath, and temperature control was by means of a mercury thermoregulator. The iron pipes containing the reaction cells were attached to a chain and sprocket wheel arrangement which rotated the iron pipes end over end in the bath, thus stirring the reaction tubes and the bath. The bath was allowed to heat up about 15° above the controlled temperature just before placing the stirrer and iron pipes therein. This reduced the time necessary to bring the reaction cells up to the high temperature. At the end of a reaction period, usually two hours, the reaction was quenched by cooling the pipes rapidly in cold water. The reaction tubes were placed in a one cm. Beckman cell holder drilled out to hold the cylindrical tubes. The absorption spectrum of the iron (III)–sulfate system is dependent upon temperature. Optical density measurements between 340 and 410 mμ were made using a cell compartment thermostated at 33°. As compared to flat faced cells, the blank optical densities of the tubular reaction cells containing either 1 *F* sulfuric acid or water were about 0.180 to 0.080, depending on the wave length. Rough values for the effective extinction coefficient, ϵl in the expression $D = c\epsilon l$ are 1300, 200 and 36 at wave lengths of 340, 375 and 400 mμ, respectively. The reaction cells were calibrated after each reaction by measuring the absorption spectra of ferric ammonium sulfate solutions in the same sulfuric acid medium. We are indebted to Mr. John Andelin who constructed the high temperature bath and made a few preliminary runs.

The room temperature reactions, which were very slow, were carried out in Pyrex absorption cells, 5 cm. in diameter by 10 cm. long, with Corex windows. It was possible to make measurements at 310 mμ, where the complex has its maximum absorption. The cells had a total volume of 150–175 ml., and about 100 ml. of solution was used. Oxygen was added and the cells sealed as described above. The absorption cells were rotated slowly in a water-bath at 30.5°. At intervals of several hours, they were removed for optical density measurements and then replaced in the bath.

In both temperature ranges, the pressure or partial pressure of oxygen was essentially constant because there was a sufficiently large gas space above the solution.

Special care was taken to remove dust particles and traces of iron salts from the reaction vessels. The inside of the vessel was washed with hot aqua regia or nitric acid, thoroughly rinsed with distilled water, dried in an oven, and then protected from dust until the reaction solution was placed in it.

Results

Effects of $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ Concentrations. (a) High Temperatures.—In the range 140–180°, at ferrous ion formal concentrations between 0.00100 and 0.0250 *F*, the oxygenation was found to proceed by two independent reaction paths—one first order in ferrous ion and in oxygen, and one second order in ferrous ion and first order in oxygen—that is, according to the rate law

$$-\frac{\mathrm{d}\ln(\mathrm{Fe^{II}})}{\mathrm{d}t} = k_\mathrm{b}P_{\mathrm{O_2}} + k_\mathrm{t}(\mathrm{Fe^{II}})P_{\mathrm{O_2}} \qquad (3)$$

where k_b and k_t may be functions of the sulfate and hydrogen ion concentrations as well. This rate law accounts for the change in rate during the course of a reaction and for the variation of initial rate with initial concentration. Added $\mathrm{Fe^{III}}$ does not affect the rate.

Since the oxygen pressure remains constant during a reaction, it would be expected that plots of $\log (\mathrm{Fe^{II}})_\mathrm{i}/(\mathrm{Fe^{II}})_t$ *vs.* t would be linear for a first-order dependence on ferrous ion. $(\mathrm{Fe^{II}})_\mathrm{i}$ and $(\mathrm{Fe^{II}})_t$ are the ferrous ion concentrations initially and at time t. Figure 1 shows that these plots are concave downward. However, plots of $1/(\mathrm{Fe^{II}})$ *vs.* t are concave upward.

The constants k_b and k_t were evaluated as follows. An apparent first-order rate constant, k', is defined by

$$k' = \frac{-\ln(\mathrm{Fe^{II}})_{t_2}/(\mathrm{Fe^{II}})_{t_1}}{t_2 - t_1}$$

for various times of reaction, where the interval between t_2 and t_1 is 1 hr. According to (3)

$$k' = k_\mathrm{b}P_{\mathrm{O_2}} + k_\mathrm{t}(\mathrm{Fe^{II}})P_{\mathrm{O_2}}$$

The quantity k' is taken to apply to the average of $(\mathrm{Fe^{II}})_{t_2}$ and $(\mathrm{Fe^{II}})_{t_1}$; plots of k' *vs.* $(\mathrm{Fe^{II}})$ were linear, as expected from (3), and were extrapolated to the initial ferrous ion concentration to give k'_i,

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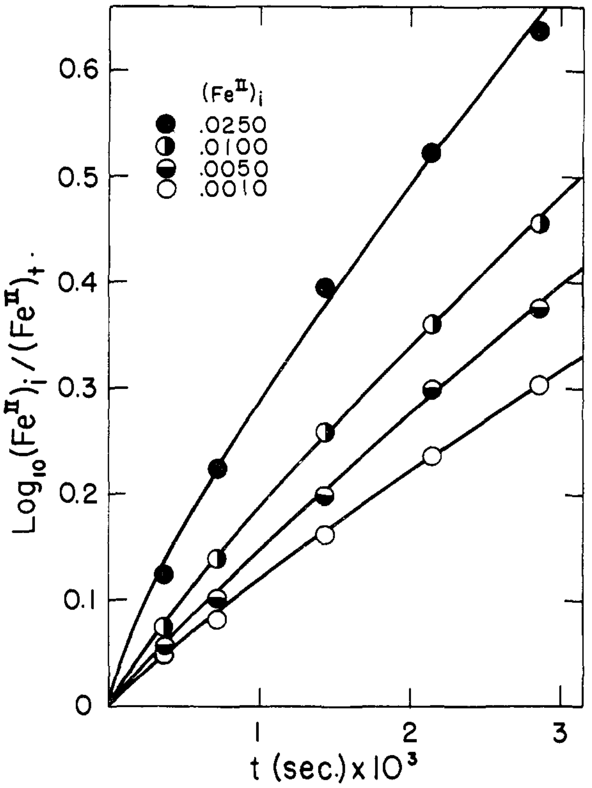

Fig. 1.—First-order plots for typical high temperature reactions (159°, 1.00 F H_2SO_4, in oxygen).

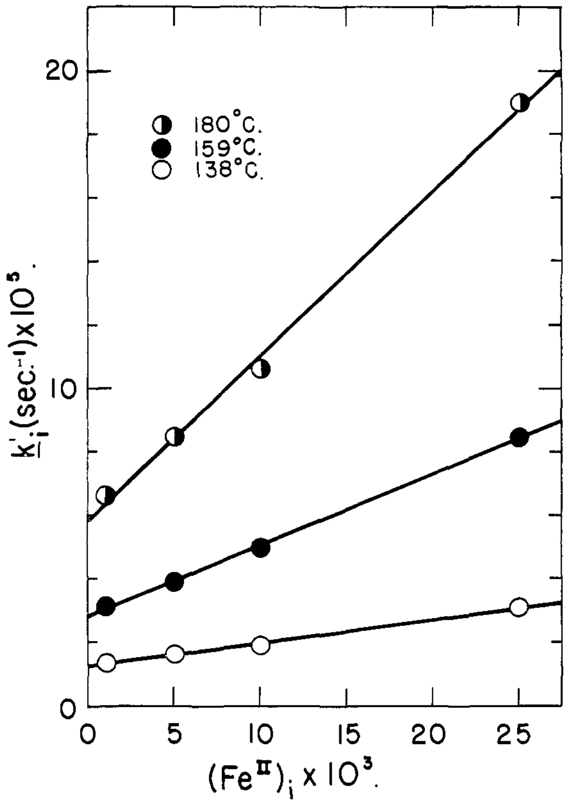

Fig. 2.—Variation of initial d ln $(Fe^{II})/dt$ with $(Fe^{II})_i$.

the initial apparent first-order constant. Values of k'_i at the same initial ferrous ion concentrations and temperatures were averaged and the averages plotted against the initial ferrous ion concentration. The straight lines obtained confirm equation 3 and are exhibited in Fig. 2. The resulting values of k_b and k_t are given in Table I. Activation energies of 13.4 (± 2) and 16.3 (+ 2) kcal. were obtained for the second-order and third-order paths, respectively, from plots of log k vs. $1/T$. The points fit on the appropriate straight lines to ±15% giving rise to the indicated uncertainties.

TABLE I

HIGH TEMPERATURE RATE AND CONSTANTS

Initial Fe^{II} (mole l.$^{-1}$)	0.00100	0.00200	0.00500	0.0100	0.0250		
T, °C.			k_i' (sec.$^{-1}$) × 10^5			k_b^{a} (sec.$^{-1}$ atm.$^{-1}$) × 10^5	k_t^{a} (sec.$^{-1}$ atm.$^{-1}$ M^{-1}) × 10^3
138	1.38		1.65	1.86	3.14	0.89	0.55
159	3.11		3.88	5.00	8.50	1.93	1.60
161	3.02	3.16	3.52	4.72		1.90	1.33
180	6.65		8.44	10.6	19.0	3.84	3.40

[a] P_{O_2} calculated from initial pressure of one atmosphere at room temperature assuming perfect gas law.

Inhibition of the reaction by ferric ion was not found. At 160° in 1.00 F H_2SO_4 with an oxygen atmosphere, the reaction in solutions initially 0.00500 F in ferrous ion and 0.00100, 0.00500, 0.0100 and 0.0200 F in ferric ion were unaffected by the added ferric ion within the experimental error of 5%. Solutions initially 0.00100 and 0.00200 F in ferrous ion containing 0.0100 F ferric ion initially gave no indication of ferric ion inhibition.

(b) Room Temperature.—The values for k_b and k_t at 30° predicted by extrapolation of the high temperature measurements are 2.5 × 10^{-8} sec.$^{-1}$ atm.$^{-1}$ and 3.5 × 10^{-7} sec.$^{-1}$ M^{-1} atm.$^{-1}$ (M = mole liter^{-1}). This suggested that the second-order path would make a contribution to the rate equal to that of the third-order path for (Fe^{II}) = 0.07 M. Previous investigators have worked at concentrations of 0.15–0.20 M,[6] 0.02–0.46 M,[4] and 0.01–0.3 M.[7] For the present investigations, measurements were obtained for only a few per cent. reaction, and the initial rate was determined from a plot of (Fe^{III}) vs. t. The initial rates were plotted as $-d\ln(Fe^{II})/dt$ vs. $(Fe^{II})_i$; the intercepts, which should have been $k_bP_{O_2}$, were smaller than the experimental error and oxygen independent. In 1.00 F H_2SO_4, k_t = 2.78 × 10^{-6} sec.$^{-1}$ M^{-1} atm.$^{-1}$ and k_b = 3 × 10^{-10} sec.$^{-1}$ atm.$^{-1}$ from rates obtained at four ferrous ion concentrations. The small contribution from the path first order in ferrous ion could be due partially to the first-order ferrous path found at high temperatures. The erratic behavior, however, indicates that this contribution is a combination of experimental error and small amounts of impurities. Values of k_t at 30.5° in two sulfuric acid–sodium sulfate solutions in air and oxygen are given in Table II.

Effect of Glass Surface.—Studies with added Pyrex glass wool showed that catalysis by the walls of the reaction cells was probably not important. The first experiments at 140–180° gave erratic results, with some reactions proceeding very

TABLE II

RATE DATA AT 30.5°

$(Fe^{II})_i$, F	$-d(Fe^{II})/dt$ air ($\times 10^{12}$)	(M sec.$^{-1}$) oxygen ($\times 10^{12}$)	Ratio of rates (oxygen/air)
	1.00 F H_2SO_4		
0.00100	6.62	6.55	
.00500	17.8	66.1	
.0100	55.0	284	
.0200	224	1130	
[a] l_t (sec.$^{-1}$ M^{-1})	5.47 × 10^{-7}	2.78 × 10^{-6}	5.1
l_b (sec.$^{-1}$)	3.9 × 10^{-10}	~0	0
	0.226 F H_2SO_4 and 0.354 F Na_2SO_4		
$(Fe^{II})_i$, F	air ($\times 10^{12}$)	oxygen ($\times 10^{12}$)	
0.00100	4.86	8.68	
.00500	44.5	143	
.0100	139	540	
.0200	545	2320	
l_t (sec.$^{-1}$ M^{-1})	1.18 × 10^{-6}	5.65 × 10^{-6}	4.8
l_b (sec.$^{-1}$)	3.1 × 10^{-9}	1.7 × 10^{-9}	0.5

[a] $-d(Fe^{++})/dt = l_b(Fe^{II}) + l_t(Fe^{II})^2$.

rapidly. Fairly reproducible results were obtained when the glass wool was heated to 500° in an oven for one-half hour, washed in hot aqua regia, rinsed, dried and transferred to the reaction cell with a glass rod. The glass wool could be centrifuged to the bottom of the cell for optical measurements.

The surface area[3] of the glass wool is estimated as 2300 cm.^{2} g.$^{-1}$. The additional surface area due to the glass wool was around three times the total inside wall area of a reaction cell. With $(Fe^{II})_i = 0.001$ to 0.005 M, in oxygen, the ratio of reaction rates in the presence and absence of glass wool varied in an erratic fashion between 1.3 and 1. Thus it appears that the wall reaction was probably never more than 10% of the homogeneous reaction in the unpacked cells. Reaction rates in unpacked cells were more reproducible than in packed cells, suggesting that the cleaning procedure was effective and reproducible for the glass walls of the cells.

Experiments at 30.5° with added glass wool were carried out in glass stoppered bottles and the solutions siphoned back and forth between optical cells with an all-glass siphon system. With $(Fe^{II})_i$ between 0.001 and 0.02 M, there was less than 1% effect that could be attributed to the walls of the optical cells.

Effect of Oxygen Pressure.—The first results obtained at 30.5° for the ratio of reaction rates in oxygen and in air at 1 atm. pressure were not the expected 4.76:1. A long and tedious set of measurements indicated that there was a reaction path that was first order in ferrous ion and zero order in oxygen and a reaction path that was second order in ferrous ion and first order in oxygen. A great deal of time was wasted before it was discovered that the commercial distilled water being used contained traces of cupric ion, which was responsible for the oxygen independent path.

At a fixed oxygen partial pressure, we may define apparent first- and second-order rate constants, referring to the dependence of rate on (Fe^{II}); $-d(Fe^{II})/dt = l_b(Fe^{II}) + l_t(Fe^{II})^2$. In redistilled water, containing no significant Cu^{II}, the ratio of l_t in oxygen and air was evaluated as 5.1 in 1.00 F H_2SO_4 and 4.8 in a solution 0.226 F in H_2SO_4 and 0.354 F in Na_2SO_4, whereas the quantity l_b was very small and evidently inversely dependent on oxygen pressure (Table II). It seems probable that the apparent first-order path is a residual effect due to impurities and experimental error; the main part of the reaction proceeds by the rate law, $-d(Fe^{II})/dt = l_t(Fe^{II})^2 = k_t(Fe^{II})^2 P_{O_2}$.

The oxygen dependence was investigated at 160° in 1.00 F H_2SO_4, where reaction paths first and second order in ferrous ion had been found to occur. One run at each of two initial ferrous ion concentrations in air and oxygen was made. The ratio of the l_t values for the path second order in ferrous ion was 5.4 and the ratio of the l_b values for the path first order in ferrous ion was 3.5. The value of 3.5 is not entirely satisfactory. These reactions at high temperatures were carried out using the same 1.00 F H_2SO_4 that was used at low temperatures, and it is known definitely that cupric ion is in very low concentration ($\sim 1 \times 10^{-7}$ F). The reaction between cupric ion and ferrous ion, which is a reasonable first step for cupric ion catalysis, would probably not be favored by an increase in temperature. The fact that the ratio of rate in oxygen to rate in air is not erratic and is 3.5 indicates that some of the path first order in ferrous ion must be oxygen dependent. We believe that the data indicate that the main part of the term in the rate law that is first order in (Fe^{II}) is also first order in oxygen. The discrepancy between 3.5 and the expected 4.8 may be partially due to impurities. It may also be partially due to errors in determining both l_b and l_t from the data on change in initial rate with $(Fe^{II})_i$ at any one oxygen pressure. The fact that the ratio, 5.4, of l_t in oxygen and air is higher than expected is consistent with this possibility.

Effect of Sulfate and Hydrogen Ion.—The effects of varying the sulfate ion at approximately constant hydrogen ion concentration and varying the hydrogen ion at relatively constant sulfate ion concentrations have been studied at 30.5° in one atmosphere of oxygen in solutions 0.0200 and 0.0400 F in ferrous ion. Stock solutions were prepared by dissolving various amounts of sodium sulfate and sulfuric acid in water that had been redistilled to remove traces of cupric ion. The solutions were kept at an ionic strength of 1.0–1.3 with sodium perchlorate. These results are uncertain in that a value for the second ionization constant for sulfuric acid must be chosen. We have taken this value to be 0.075 at an ionic strength of 1.0 (sodium perchlorate).[10] The dependence of the third-order rate constant k_t on sulfate ion is seen in Fig. 3. The hydrogen ion was varied from 0.066 to 0.099 M in this series but, as will be seen later, this will have little effect. The rate constant increases at a decreasing rate as the sulfate ion concentration is increased. The increase in the sulfate ion concentration and the slight increase in optical density of the reaction solution due to the large amounts of ferrous ammonium sulfate added have been taken into account.

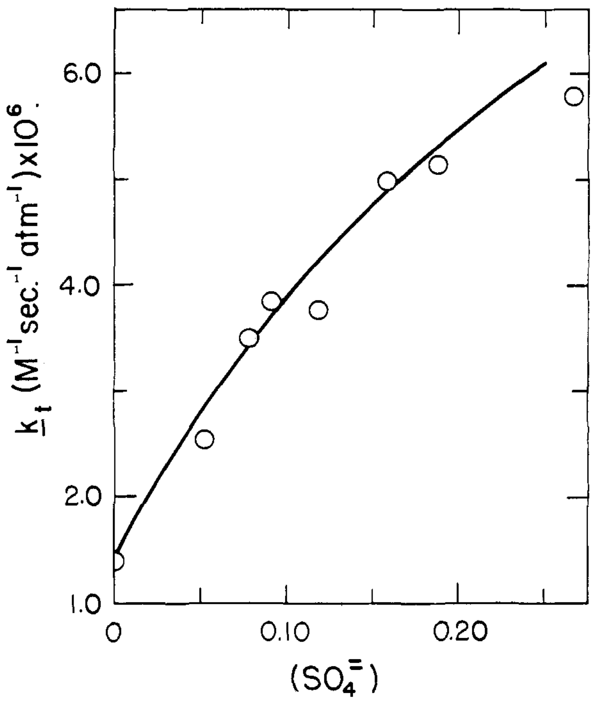

Fig. 3.—Dependence of termolecular rate constant at 30.5° on sulfate ion concentration. Reactions in oxygen at one atmosphere pressure. The formal concentrations of the various added chemicals, and the calculated concentrations of some of the ions (assuming $K_{HSO_4^-} = 0.075$) are displayed below. $\mu = 1.0–1.3$ (sodium perchlorate).

(H_2SO_4), F	(Na_2SO_4), F	(Fe^{II}), F	($SO_4^=$), M	(H^+), M	(HSO_4^-), M
0.068	0	0.020	0.052	0.080	0.056
		.040	.078	.066	.070
.094	.061	.020	.091	.084	.104
		.040	.118	.071	.117
.135	.166	.020	.158	.087	.183
		.040	.118	.077	.193
.226	.354	.020	.267	.099	.353

The increase in the rate constant can be explained by the following argument. At zero sulfate ion concentration, the path second order in ferrous ion should be the same as the path in perchloric acid, where little complexing is to be expected. From data of George,[7] the constant for this reaction is found to be 1.4 × 10^{-6} M^{-1} atm.$^{-1}$ sec.$^{-1}$ in 0.083 F $HClO_4$ at 30° and an ionic strength of 1.0. When this value is placed on Fig. 3, it is possible to draw a smooth curve through the points. A reasonable mechanism for sulfate ion catalysis would seem to be

$$2Fe^{++} + O_2 \xrightarrow{k_u} 2Fe^{III} + H_2O_2 \qquad (4)$$

as an uncatalyzed rate step, and

$$Fe^{++} + SO_4^= \overset{K}{\rightleftarrows} Fe^{++}SO_4^= \qquad (5)$$

$$Fe^{++}SO_4^= + Fe^{++} + O_2 \xrightarrow{k_s} 2Fe^{III} + H_2O_2 + SO_4^= \qquad (6)$$

for the sulfate-catalyzed rate step. This mechanism would lead to the rate expression

$$\frac{-d(Fe^{II})}{dt} = k_u(Fe^{++})^2P_{O_2} + k_s(FeSO_4)(Fe^{++})P_{O_2} = k_t(Fe^{II})^2P_{O_2} \qquad (7)$$

If all ferrous ion is either uncomplexed or as the ferrous-sulfate complex, the following expressions may be obtained, where (Fe^{II}) is the formal ferrous ion concentration.

$$\frac{(FeSO_4)}{(Fe^{II})} = \frac{K(SO_4^=)}{1 + K(SO_4^=)} \qquad \frac{(Fe^{++})}{(Fe^{II})} = \frac{1}{1 + K(SO_4^=)}$$

Substituting these expressions into (7), one obtains

$$k_t = \frac{k_u + k_sK(SO_4^=)}{1 + K(SO_4^=)^2} \qquad (8)$$

By setting $k_u = 1.4 \times 10^{-6}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$ as found by George, and assuming the sulfate ion concentration is not appreciably affected by the ferrous sulfate complex, expression (8) may be solved numerically for k_s and K by using values of k_t and ($SO_4^=$) from Fig. 3. Values obtained were $K = 1.1 \pm 0.2$ M^{-1} and $k_3 = 3.1 \pm 0.5 \times 10^{-6}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$. The curve shown in Fig. 3 is the theoretical curve drawn from (8) with these values.

The results obtained by varying the hydrogen ion concentration are shown in Table III. The hydrogen ion dependence of the reaction is uncertain from these experiments in that the sulfate ion concentration has not been controlled as well as desired. This makes detailed kinetic interpretation difficult. However, as the hydrogen ion concentration is decreased by a factor of 75 from 1.032 to 0.014, the rate constant at most doubles. Also, the rate constant does not change drastically over the hydrogen ion concentrations which were obtained in the sulfate dependence experiments. We have no satisfactory explanation for the observed small dependence upon hydrogen ion concentration. A generally similar dependence of the termolecular rate constant on H^+ is observed in perchlorate media.[7]

TABLE III

HYDROGEN ION DEPENDENCE

H_2SO_4, F	Na_2SO_4, F	Fe(II), F	($SO_4^=$), M	(H^+), M	(HSO_4^-), M	k_t (M^{-1} sec.$^{-1}$ atm.$^-$) × 10^6
1.00	0.0	0.0200	0.072	1.032	0.968	2.78
0.466	.040	.0200	.075	0.461	.471	3.17
		.0400	.086	.432	.500	3.00
.094	.061	.0200	.091	.084	.104	3.86
		.0400	.118	.071	.117	3.78
.0203	.0664	.0200	.104	.017	.023	5.28
		.0400	.141	.014	.026	5.05

All rate determinations in this investigation were made on solutions of ferrous ammonium sulfate. By adding an equal concentration of ammonium sulfate to a typical high temperature reaction in 1.00 F H_2SO_4 under oxygen, the ammonium ion was shown to be without effect on the reaction rate.

Possible Effects of Organic Impurities.—In the high temperature range, it was thought that residual organic dust impurities might participate in induced reactions, or otherwise enter into the reaction and be destroyed in the process. To check on this possibility, solutions with $(\mathrm{Fe^{II}})_i = 0.001$ to 0.005 *F* in 1.00 *F* sulfuric acid were heated at 160° in oxygen to about 60% reaction. The tubes were then carefully opened, and a small, known volume of a concentrated ferrous ion solution was added. The tubes were then resealed in oxygen and reheated. The observed rate constants were the same before and after addition of the concentrated ferrous ion solution. Since there was no decrease in rate constant after addition of the concentrated ferrous ion solution, either reaction with organic dust impurities is not occurring, or the concentration of these impurities is too large to be appreciably reduced by the reaction.

Effect of Cu(II).—As described previously, the anomalous results first obtained at 30.5° led us to suspect $\mathrm{Cu^{II}}$ as an impurity. Trace analyses for $\mathrm{Cu^{II}}$ were therefore made using a spectrophotometric method based on the dithizone–cupric ion complex.[11] Sulfuric acid, sodium sulfate, ferrous ammonium sulfate and sodium perchlorate solutions were found not to contain significant concentrations of cupric ion. However, commercial distilled water contained concentrations of *ca.* 2×10^{-6} *F* $\mathrm{Cu^{II}}$. In redistilled water, the cupric ion concentration was reduced at least twenty times to a value which would not significantly affect the rate.

At 30.5° in sulfuric acid–sodium sulfate solutions, cupric ion catalyzes the ferrous ion–oxygen reaction by a reaction path first order in ferrous ion, first order in cupric ion and zero order in oxygen pressure. These results have been obtained in a stock solution 0.226 *F* in H_2SO_4 and 0.354 *F* in Na_2SO_4, which has $(\mathrm{H^+}) = 0.11$ *M*, $(\mathrm{HSO_4^-}) = 0.34$ and $(\mathrm{SO_4^{=}}) = 0.24$.

In these solutions, increasing the cupric ion concentration increases the rate of the reaction path first order in ferrous ion. It was found that the measured rate is a linear function of the total cupric ion concentration for reactions with $(\mathrm{Fe^{II}})_i = 0.00100$ *F* in air at one atmosphere. In reactions containing the relatively high total cupric ion concentration of 1.1×10^{-5} *F*, the rate is the same in air and oxygen. The rate law for this situation at given sulfate and hydrogen ion concentrations is

$$-\mathrm{d(Fe^{II})}/\mathrm{d}t = k_t(\mathrm{Fe^{II}})^2 P_{\mathrm{O_2}} + 4k_9(\mathrm{Fe^{II}})(\mathrm{Cu^{II}})$$

The above equation with $k_9 = 1.9 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$ and $k_t = 1.5 \times 10^{-5}\ M^{-1}$ atm.$^{-1}$ sec.$^{-1}$ fits the data to ±5%.

Since the concentrations of cupric and ferric ions are relatively low, the catalysis may be explained by the following reactions postulated by Cher and Davidson[3] and many previous workers.

$$\mathrm{Cu^{II} + Fe^{II} \xrightarrow{k_9} Cu^{I} + Fe^{III}} \qquad (9)$$

$$\mathrm{Cu^{I} + O_2 \longrightarrow Cu^{II} + HO_2} \qquad (10)$$

It is assumed that the first reaction is the rate step and the second reaction is very rapid. The HO_2 reacts further with $\mathrm{Fe^{II}}$ as in the Weiss mechanism.[8]

Discussion

The activation energy for the bimolecular reaction measured between 140 and 180° is 13.4 (± 2) kcal. However, the upper limit for k_b at 30.5° combined with the average value, $k_b = 1.9 \times 10^{-5}$ sec.$^{-1}$ atm.$^{-1}$ at 160°, implies that $E_a > 22$ kcal. The activation energy for the termolecular reaction observed at high temperatures is 16.3 (± 2) kcal. The values at 160 and 30° imply $E_a = 12.6$ kcal. George[7] reports $E_A = 17.4$ kcal, for the termolecular path between 20 and 40° in 0.50 *F* $HClO_4$. The possibility of unknown experimental errors cannot, of course, be excluded. However, it would not be surprising if the activation energy for either reaction path were dependent on temperature. This is especially likely because there is probably a very marked change in the concentrations and activity coefficients of the ionic species present in 1*F* H_2SO_4 between 30° and the range 140–180°.

The experimental results do not, of course, distinguish between the alternative intermediate HO_2 and $\mathrm{Fe^{IV}}$ (reactions 1a and b) for the bimolecular reaction path. The Weiss mechanism[8] involves the former intermediate. In this case, the complete reaction path is

$$\mathrm{Fe^{II} + O_2 \longrightarrow Fe^{III} + HO_2} \qquad (1a)$$

$$\mathrm{Fe^{II} + HO_2 \longrightarrow Fe^{III} + H_2O_2} \qquad (11)$$

$$\mathrm{Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + OH + OH^-} \qquad (12)$$

$$\mathrm{Fe^{II} + OH \longrightarrow Fe^{III} + H_2O} \qquad (13)$$

The observed values of k_b are four times the rate constant for reaction (1a) for this mechanism.

Experiments in this Laboratory have shown that in a pyrophosphate medium, the rate of oxygenation is first order in $\mathrm{Fe^{II}}$ and first order in oxygen,[2] and faster than the corresponding reaction rate in a phosphate medium. Weiss[9] has reported that the reaction is bimolecular with respect to $\mathrm{Fe^{II}}$ and O_2 in the presence of fluoride. Posner[5] reports a bimolecular reaction in 5–8 *F* HCl at room temperature, and the reaction rate decreased markedly with acidity. As discussed below, the data of McBain[4] indicate that the reaction is principally termolecular in 1 *F* HCl. In a perchlorate medium,[7] the reaction path at room temperature is exclusively termolecular, and no investigations have been made at high temperature.

Weiss[9] has proposed essentially the following as a model of the transition state

$$[\mathrm{X{-}{-}{-}Fe^{II}{-}{-}{-}O_2}] \longleftrightarrow [\mathrm{X{-}{-}{-}Fe^{III}{-}{-}{-}O_2^-}]$$

The transition state is stabilized by groups, X, which form complexes with tripositive iron. The equilibrium constants for the reaction

$$\mathrm{Fe^{+++} + X^{-n} \rightleftarrows FeX^{3-n}}$$

for $\mathrm{H_2P_2O_7^{=}}$,[12] $\mathrm{F^-}$,[13] $\mathrm{H_2PO_4^-}$,[14] $\mathrm{SO_4^{=}}$,[10] $\mathrm{Cl^-}$,[15] $\mathrm{ClO_4^-}$,[16] in the neighborhood of 25° are: 10^6, 5×10^5, 1.4×10^3, 100, 4.1, 1–3 mole^{-1} liter, respec-

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[11] E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1950, p. 295.

[12] Preliminary estimate based on work in this Laboratory.

[13] H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949).

[14] T. Yamane and N. Davidson, to be published.

[15] M. W. Lister and D. E. Rivington, *Can. J. Chem.*, **33**, 1603 (1955).

[16] K. W. Sykes, *Chem. Soc. Special Pub. No. 1*, 64 (1954).

tively. Thus, in the presence of the strong complexes, the oxygenation is bimolecular at room temperature. For the complexing agents of moderate strength, $SO_4^=$ and Cl^-, the reaction is termolecular at room temperature and moderate (< 1 F) concentration of the complexing anions. A bimolecular reaction occurs in more extreme conditions—at high temperatures in 1 F H_2SO_4 or in 5 F HCl at room temperature. At room temperature in perchlorate media, the oxygenation is termolecular; it is not known whether a bimolecular reaction will occur for more extreme conditions. Suitable data for a quantitative comparison are not available, but the relative reaction rates for the bimolecular path generally parallel the complexing constants quoted above.

The rate-determining step for the termolecular path is probably

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

followed by reactions (7) and (8). The observed values of k_t are therefore twice the rate constant of the above reaction. Two possible detailed models for reaction (2) are

$$(H_2O_2)_5Fe^{II}OH_2{}^{++} + O{=}O + H_2OFe^{II}(OH_2)_5{}^{++} \longrightarrow$$
$$(H_2O_2)_5Fe^{III}OH^{++} + H_2O_2 + HOFe^{III}(OH_2)_5{}^{++} \qquad (2')$$

$$(H_2O)_6Fe^{++} + O{=}O + Fe(H_2O)_6 \rightleftarrows$$
$$(H_2O)_5Fe^{II}\ldots.O{=}O\ldots Fe^{II}(H_2O)_5{}^{++++} \longrightarrow$$
$$(H_2O)_5Fe^{III}\text{–}O\text{–}O\text{–}Fe^{III}(H_2O)_5{}^{++++} \longrightarrow \qquad 2('')$$
$$(H_2O)_6Fe^{+++} + H_2O_2 + Fe(H_2O)_6{}^{+++}$$

Mechanism (2′) involves a hydrogen atom transfer from the water molecules of the coördination sphere of Fe^{++}. In mechanism (2″), an O_2 molecule is directly coördinated to two Fe^{++} ions, and a peroxide bridge between two Fe^{+++} ions is formed. It may be recalled that a peroxy complex of Fe^{III}, $Fe(O_2H)^{++}$, is known.[17,18] If (2′) were correct, there should be a marked hydrogen isotope effect and a significant decrease in reaction rate in D_2O, whereas this should not be the case for (2″). Evidence of this nature in favor of a hydrogen atom transfer mechanism for the Fe^{++}, Fe^{+++} electron exchange has recently been reported.[19] Evidence that there is no significant hydrogen isotope effect in the similiar Pu^{III}–Pu^{IV} oxygenation has been found recently.[18] In either case, it is plausible that sulfate ion would accelerate the rate because of complex ion formation in the transition state. Thus for case (2″), the transition state would be

$$(H_2O)_4(SO_4)Fe\text{–}O\text{–}O\text{–}Fe(H_2O)_5{}^{+4}$$

No independent evidence is available to compare with the deduction from the kinetic data that the complex constant of Fe^{++} with $SO_4^=$ is 1.1 mole^{-1} liter. The value is about as expected for these ions for an ionic strength of 1.0, however.

The termolecular rate constant k_t at 30.5° in 1 F H_2SO_4 found in this study, 2.78×10^{-6} M^{-1} atm.$^{-1}$ sec.$^{-1}$, agrees well with values reported by other investigators. Lamb and Elder[6] found 4.0×10^{-6} and McBain[4] reported 1.1×10^{-6}, in both cases at 30° in 1 F H_2SO_4. (The corresponding comparison made by George[7] between rates in $HClO_4$ and in H_2SO_4 is slightly erroneous in that Lamb and Elder's results were not corrected from 1 atm. air to 1 atm. O_2.) We find that the data of McBain in 1 F HCl fit a termolecular rate law much better than a bimolecular rate law; the rate constant (apparently at 30°) is 6.5×10^{-6} M^{-1} atm.$^{-1}$ sec.$^{-1}$.

The rate constant for the first step in the cupric ion catalyzed reaction is 1.9×10^{-3} M^{-1} sec.$^{-1}$

$$Fe^{II} + Cu^{II} \longrightarrow Fe^{III} + Cu^{I} \qquad (9)$$

in 0.226 F H_2SO_4, 0.354 F Na_2SO_4. The corresponding value in 0.434 F H_3PO_4, 0.302 F $H_2PO_4^-$ is 2.8×10^{-1}. This shows that phosphate ion complexes the iron in the transition state for reaction (9). Since sulfate is a moderately strong complexing anion for Fe^{+++}, it may be assumed that $SO_4^=$ can also participate in the transition state for reaction (9). Unfortunately, no data to test this prediction were obtained.

George[7] reports that the Fe^{II}, O_2 reaction in perchloric acid is only slightly catalyzed by Cu^{II}, and that the catalyzed reaction is second order in Fe^{II}. The smallness of the catalytic effect may in part be due to the slowness of reaction (9) in $HClO_4$. There is however an additional consideration. Cher and Davidson[3] observed that at high Cu^{II} concentrations, the mechanism of the Fe^{II}, O_2 reaction was

$$Fe^{II} + Cu^{II} \overset{K_9}{\rightleftarrows} Fe^{III} + Cu^{I} \qquad (9)$$

$$Cu^{I} + O_2 \overset{K_{10}}{\rightleftarrows} Cu^{II} + HO_2 \qquad (10)$$

$$Fe^{II} + HO_2 \xrightarrow{k_{11}} Fe^{III} + H_2O_2 \qquad (11)$$

The corresponding rate expression is $-d(Fe^{II})/dt = 4\,k_{11}K_9K_{10}\,(Fe^{II})^2P_{O_2}/(Fe^{III})$, and the rate is independent of Cu^{II} concentration. K_9K_{10} is actually the equilibrium constant for the reaction

$$Fe^{II} + O_2 \rightleftarrows Fe^{III} + HO_2 \qquad (12)$$

The value of this equilibrium quotient in 1 F $HClO_4$ may be estimated as 3×10^{-4} of its value in 0.43 F H_3PO_4, 0.30 F $H_2PO_4^-$ from the formation constants of $Fe(H_2PO_4)^{++}$ and $Fe(H_2PO_4)_2{}^+$ (1.4×10^3 mole^{-1} liter and 3.4×10^4 mole^{-2} liter^2).[14] Reaction (10) is a fast, exothermic reaction and possibly not greatly affected by complexing anions. On this basis, we estimate from the results of Cher and Davidson[3] that the rate law for the copper catalyzed reaction in 1 F $HClO_4$ is $-d(Fe^{II})dt = 8 \times 10^{-7}\,(Fe^{II})^2P_{O_2}/(Fe^{III})$; the rate law for the uncatalyzed reaction is $2 \times 10^{-6}(Fe^{II})^2P_{O_2}$. It is not expected that the above calculation is very reliable, but it does suggest that after the accumulation of some Fe^{III} in the system, the copper catalyzed reaction might indeed be rather insignificant in comparison to the uncatalyzed *termolecular* reaction.

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[17] M. G. Evans, D. George and N. Uri, *Trans. Faraday Soc.*, **45**, 230 (1949).

[18] We are indebted to Dr. T. W. Newton for some interesting corespondence regarding the possibility of (2″).

[19] J. Hudis and R. W. Dodson, THIS JOURNAL, **78**, 911 (1956).