The Oxidation of Ferrous Perchlorate by Molecular Oxygen.

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The kinetics of the oxidation of ferrous ion by molecular oxygen, in perchloric acid solution, have been studied over a temperature range 25—40° at various pH's and ionic strengths (adjusted by addition of sodium perchlorate). With air and oxygen at atmospheric pressure, and oxygen at 100—130 atm., a special apparatus being used, the same kinetics were obtained, *viz.*,

$$-d[Fe^{2+}]/dt = k_{exp.}[Fe^{2+}]^2[O_2]$$

The overall third-order velocity constant $k_{exp.}$ increased slightly with a decrease of hydrogen-ion concentration according to an empirical equation $k_{exp.} \propto [H^+]^{-0{\cdot}23}$; $k_{exp.}$ also increases slightly as the ionic strength is increased. The possibility that these kinetics depend on either the coupled oxidation of organic impurities, or catalysis by trace metals, is shown to be very unlikely. Cupric perchlorate catalysed the oxidation, but the effect was small, becoming maximal at 0·15—0·20M-Cu^{2+} with a 2·5-fold increase in $k_{exp.}$

The familiar electron-transfer and free-radical mechanism involving O_2^- and HO_2 cannot account for these kinetics, which favour, instead, a mechanism of the type

$$Fe^{2+} + O_2 \rightleftharpoons Fe^{2+}O_2$$

$$Fe^{2+}O_2 + H_2O,Fe^{2+} \longrightarrow FeO_2H^{2+} + HOFe^{2+}$$

The second step involves hydrogen-atom transfer from a water molecule of the co-ordination shell of one ferrous ion to a ferrous ion–oxygen complex, and amounts to the transfer of two oxidising equivalents simultaneously—one intramolecularly and one intermolecularly.

The oxidation data are discussed in relation to mechanisms recently suggested for the ferric-ion catalysed decomposition of hydrogen peroxide, because a simple radical mechanism has also been found to break down in this case.

The slow rate of oxidation of ferrous ions by molecular oxygen is probably the reason why this reaction has been investigated far less than the corresponding oxidation by hydrogen peroxide, and the ferric-ion catalysed peroxide decomposition. Yet a knowledge of its kinetics is very desirable since the reaction mechanism must be consistent with those of the other reactions, hydrogen peroxide being a two-equivalent reduction state, intermediate in the overall four-equivalent reduction of molecular oxygen to water. Identical reaction paths at certain stages of the various reactions are in fact to be expected.

Early studies showed the rate of oxidation of ferrous sulphate and bicarbonate solutions to be directly proportional to the oxygen pressure (McBain, *J. Phys. Chem.*, 1901, **5**, 623; Just, *Ber.*, 1907, **40**, 3695). A second-order reaction in ferrous ion was found in the case of the sulphate (McBain, *loc. cit.*; Ennos, *Proc. Camb. Phil. Soc.*, 1913, **17**, 182; Boselli, *J. Chim. phys.*, 1912, **10**, 49), but a first-order reaction with the bicarbonate (Just, *loc. cit.*). Lamb and Elder's more thorough investigation with ferrous sulphate confirmed these findings (*J. Amer. Chem. Soc.*, 1931, **53**, 137); and the few observations made by Pound with the nitrate and perchlorate suggest that these too show the same kinetic behaviour (*J. Phys. Chem.*, 1939, **43**, 955). In all cases the slow rate necessitated measurements corresponding to about 1% total reaction, or having excessively long reaction times of several days. The present investigation was planned to check results obtained when using 1 atm. pressure of oxygen and a sensitive colorimetric method for estimating ferric iron, against those obtained by using about 100 atm. oxygen pressure and direct titration of ferrous ion, so as to establish beyond doubt the validity of these results.

As early as 1907, Just (*loc. cit.*) discussed a reaction mechanism involving the HO_2 radical, recognising its relationship to the O_2^- ion formed when an oxygen molecule accepts an electron. Later, Weiss proposed the following sequence of reactions (*Naturwiss.*, 1935, **23**, 64):

$$\begin{aligned} Fe^{2+} + O_2 &\overset{k_a}{\rightleftharpoons} Fe^{3+} + O_2^- \\ H^+ + O_2^- &\rightleftharpoons HO_2 \\ Fe^{2+} + HO_2 &\rightleftharpoons Fe^{3+} + O_2H^- \\ H^+ + O_2H^- &\rightleftharpoons H_2O_2 \\ 2Fe^{2+} + H_2O_2 &\longrightarrow 2Fe^{3+} + 2OH^- \end{aligned}$$

If the first of these is the rate-determining step with velocity constant k_a, then the initial oxidation rate is given by

$$-d[Fe]^{2+}/dt = k_a[Fe^{2+}][O_2] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

This is only in accord with Just's results for bicarbonate solution, and leaves unexplained the second-order dependence on ferrous-ion concentration obtained with sulphates, nitrates, and perchlorates. George (*Adv. Catalysis*, 1952, **4**, 367) directed attention to this discrepancy, and referred to the results now reported in full below. Weiss (*Experientia*, 1953, **9**, 61) has since published a revised mechanism which is referred to on p. 4358.

RESULTS

(a) *Effect of varying the Ferrous-ion Concentration.*—Initial oxidation rates were measured at two hydrogen-ion concentrations in a series of experiments with oxygen at one atmosphere pressure, in which the ferrous-ion concentration was varied by a factor of about forty. The log–log plot of rate against ferrous-ion concentration (Fig. 1) is linear with a slope of two, and so the reaction is of second order with respect to ferrous ion under these conditions. The points for the lower concentrations, less than 0·05M-Fe^{2+}, do not lie particularly well on the line, but there is no evidence of any systematic deviation. The discrepancies are probably due to the considerable error in the rate determinations under these conditions, for only about 5×10^{-6} to 5×10^{-5}M-Fe^{3+} was formed in 24 hr.

A factor which has not yet been taken into account is the change of solubility of oxygen in the reaction mixture as the concentration of ferrous salt is altered. MacArthur's measurements (*J. Phys. Chem.*, 1916, **20**, 495) on a variety of salts show that a fall in solubility, of about 16%, is to be expected over the entire range of ferrous salt concentrations employed. This would have the effect of improving the linearity of the data for 0·01M-$HClO_4$ in Fig. 1, but not that for 0·103M: in any case the effect would be very small over the most reliable range from 0·025 to 0·23M-Fe^{2+}.

Even with the highest ferrous-ion concentration used, 0·24M, as little as 3% was oxidised in the course of an experiment. Now, since traces of oxidisable organic matter are known to affect the oxidation of ferrous ion by hydrogen peroxide if molecular oxygen is present

(Baxendale, Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 155; Kolthoff and Medalia, *J. Amer. Chem. Soc.*, 1949, **71**, 3777, 3784; Barb, Baxendale, George, and Hargrave, *Trans. Faraday Soc.*, 1951, **47**, 462), it was desirable to see whether the above results were also obtained under conditions where such a complication is ruled out. Throughout an oxidation at oxygen pressures of about 100 atm. the oxidation was again found to be of second order with respect to ferrous ion as shown in Fig. 2. The slight deviations noticeable toward the end of the experiments can be attributed to the unavoidable but known fall in oxygen pressure inside the steel block containing the reaction vessel. The reaction order remains unchanged whilst at least 0·1M-ferrous ion is oxidised to ferric ion; it is therefore extremely unlikely that the kinetics depend in any way on oxidisable impurities because in the reaction with hydrogen peroxide Barb, Baxendale, George, and Hargrave (*loc. cit.*) found that traces of impurities no longer affected this reaction provided that the concentration of the reactants was above 5×10^{-5}M, *i.e.*, 0·05% of the ferrous-ion concentration employed in the present experiments.

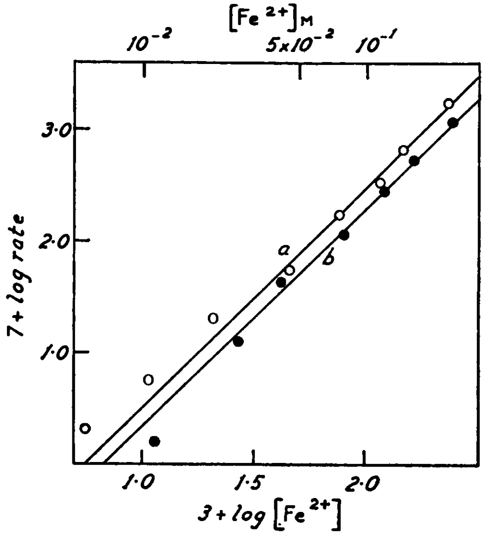


FIG. 1. *Plot of the logarithm of the rate of ferrous-ion oxidation* ($\times 10^7$) *in mole/l./hr. against the logarithm of the initial ferrous-ion concentration* ($\times 10^3$) *with oxygen at* 1 *atm. pressure, for two perchloric acid concentrations*: (a) 0·0103M *and* (b) 0·103M, *at* 25°.

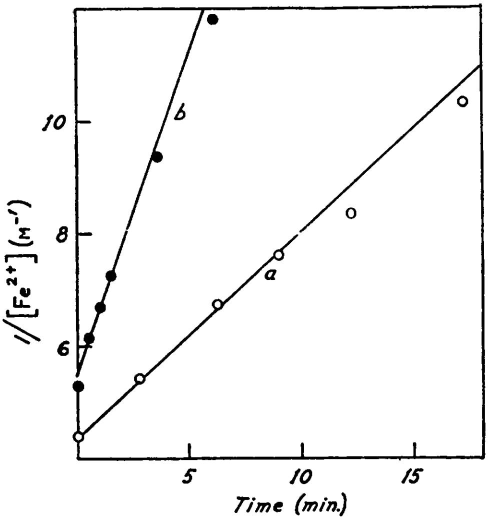


FIG. 2. *Plot of the reciprocal of the ferrous-ion concentration against time for oxidation experiments at* 35° *in* 0·51M-*perchloric acid*: (a) *Oxygen pressure* 124 *falling finally to* 103 *atm.*; (b) *Oxygen pressure* 133—130 *atm. with* $8{\cdot}3 \times 10^{-2}$M-*cupric perchlorate present in solution.*

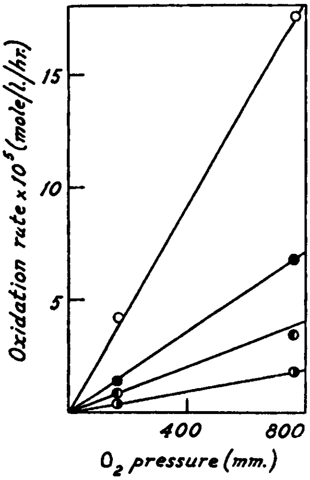


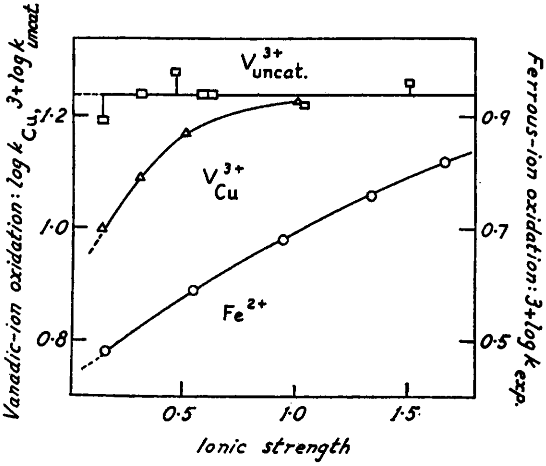
FIG. 3. *Plot of the rate of ferrous-ion oxidation* ($\times 10^5$) *in mole/l./hr. as a function of the oxygen pressure, from experiments carried out in air and in oxygen at* 25° *in* $1{\cdot}03 \times 10^{-2}$M-*perchloric acid, using four initial ferrous ion concentrations*, viz., *from top to bottom*, 0·23, 0·144, 0·115, *and* 0·077M, *respectively.*

(b) *Effect of varying the Oxygen Pressure.*—At four ferrous-ion concentrations the oxidation rate was found to be directly proportional to oxygen pressure, as shown in Fig. 3. Combining this result with that of section (a), we obtain the rate equation

$$d[Fe^{3+}]/dt = -d[Fe^{2+}]/dt = k_{exp.}\,[Fe^{2+}]^2[O_2] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

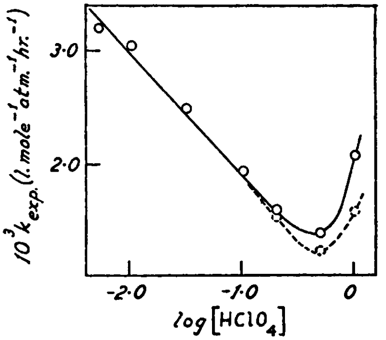
where $k_{exp.}$ is the overall third-order velocity constant. Within experimental error this same oxygen-pressure dependence holds at pressures up to 100 atm., as the following calculation shows. The results plotted in Fig. 2*a* give a bimolecular velocity constant of 0·36 l. mole^{-1} hr.$^{-1}$. Assumption of an average oxygen pressure of 113 atm. throughout the experiment gives $k_{exp.} = 0{\cdot}36/113 = 3{\cdot}2 \times 10^{-3}$ l. mole^{-1} atm.$^{-1}$ hr.$^{-1}$. At the same temperature and hydrogen-ion concentration, *i.e.*, 35° and 0·51N-HClO$_4$, the simpler technique at atmospheric pressure gave $k_{exp.} = 3{\cdot}7 \times 10^{-3}$ l. mole^{-1} atm.$^{-1}$ hr.$^{-1}$. The agreement to within 15% is very satisfactory considering the differences between the two experimental methods.

FIG. 4. *The variation of* log ($k_{exp.} \times 10^3$) * *for ferrous-ion oxidation in* 5 × 10^{-3}M-*perchloric acid in oxygen at* 1 *atm. pressure at* 25°, *as a function of the ionic strength of the solution varied by additions of sodium perchlorate.*



Similar data are also plotted for the uncatalysed oxidation of vanadic ions in 0·0125N-*perchloric acid,* log ($k_{uncat.} \times 10^3$),* *and for the same oxidation catalysed by* 10^{-4}M-*cupric ion in* 0·10N-*perchloric acid,* log ($k_{Cu} \times 10$), *both at* 25° *and* 1 *atm. pressure of oxygen* (*Ramsey, Sugimoto, and DeVorkin,* J. Amer. Chem. Soc., 1941, **63**, 3480).

FIG. 5. *The rate constant* $k_{exp.}$ ($\times 10^3$) *for ferrous-ion oxidation at* 25° *plotted against the logarithm of the perchloric acid concentration. The dotted portion of the curve passes through values of* $k_{exp.}$ *adjusted to a constant ionic strength of* 0·4.



(c) *Effect of varying the Ionic Strength of the Solution.*—The initial oxidation rates of a 4·8 × 10^{-2}M-ferrous ion solution containing 5 × 10^{-3}N-perchloric acid in oxygen at atmospheric pressure and 25° were measured with the addition of various amounts of sodium perchlorate to the solution so that the ionic strength ranged from 0·15 to 1·66. The velocity constants were calculated by equation (2) and are given in the second row of Table 1. Before the effect of ionic strength on the velocity constant can be appreciated, these values need correction for the variation of oxygen solubility with the concentration of neutral salt present. By assuming that the variation with sodium perchlorate is identical with that found by MacArthur (*loc. cit.*) with

TABLE 1. *The effect of increasing ionic strength, by addition of sodium perchlorate, on the velocity constant for ferrous-ion oxidation in* 5 × 10^{-3}M-HClO$_4$ *in oxygen at atmospheric pressure at* 25°.

Ionic strength	0·15	0·54	0·94	1·34	1·66
$10^3\,k_{exp.}$, l. mole^{-1} atm.$^{-1}$ hr.$^{-1}$	2·9	3·4	3·8	4·2	4·55
Corrected values of $10^3\,k_{exp.}$	3·0	3·9	4·75	5·8	6·6

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* These velocity constants have been corrected to allow for the variation of oxygen solubility with salt concentration (see p. 4351). The correction is not required in the copper-catalysed reaction because this is independent of oxygen pressure.

potassium nitrate, which is justified since he found that many uni-univalent salts show a very similar effect, a multiplying factor has been evaluated for each ionic strength based on the oxygen solubility at zero salt concentration as the reference value. The constants corrected in this way are given in the third row of Table 1. The variation of the logarithm of the rate with ionic strength is a little less than first power, with a slope of about 0·26 (Fig. 4); with the square root of the ionic strength the variation is rather more than first power.

(d) *Effect of varying the Perchloric Acid Concentration.*—With seven different concentrations of perchloric acid present, from 5×10^{-3} to 1·0N, initial oxidation rates in oxygen at atmospheric pressure were measured at three or four ferrous-ion concentrations ranging from 0·077 to 0·23M. In Fig. 5, the values of $k_{exp.}$ are plotted against the logarithm of the perchloric acid concentration. Those for an acid concentration of 0·1N and less correspond to an effectively constant ionic strength of 0·4, whereas above this concentration the ionic strength of the solution increases progressively to 1·3. In this range the values have therefore been adjusted according to the data in Table 1 to ionic strength 0·4, and the broken portion of the curve in Fig. 5 drawn through them; $k_{exp.}$ can be seen to increase as the acid concentration is decreased below 0·5N, and increase again as the acid concentration is increased above 0·5N. This increase at high concentration, however, is less marked than would appear if no correction were made for the change in ionic strength.

FIG. 6. *Plot of* log $k_{exp.}$ ($\times 10^3$) *for ferrous-ion oxidation in* 0·51M-*perchloric acid against the reciprocal of the absolute temperature.*

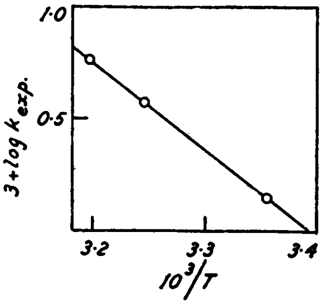
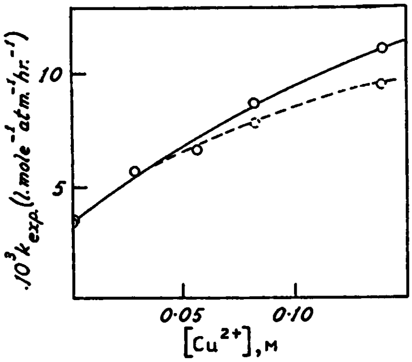


FIG. 7. *The variation of* $k_{exp.}$ ($\times 10^3$) *for the oxidation of ferrous ions in* 0·51M-*perchloric acid at* 35° *with the concentration of added cupric perchlorate. The dotted curve passes through values of* $k_{exp.}$ *adjusted to a constant ionic strength of* 1·1.



Although $k_{exp.}$ is a function of the hydrogen-ion concentration, even if the range of this is low, it is not a simple function involving an integral order, nor is it of the form $K/(K + [H^+])$, where K is an acid dissociation constant. The dependence below 0·5M-$HClO_4$ can be represented very approximately by $[H^+]^{-0·23}$, but this, of course, has no significance with regard to a kinetic mechanism.

(e) *Activation Energy for the Oxidation of Ferrous Ions by Molecular Oxygen in* 0·51N-*Perchloric Acid.*—A plot of log $k_{exp.}$ against the reciprocal of the absolute temperature is linear, as shown in Fig. 6, and from the slope the activation energy is calculated to be 17·4 kcal./mole. The particular acid concentration of 0·51N was chosen because it lies in the range where the rate varies least with changing acid concentration (see Fig. 4). In view of the slight variation of the rate with hydrogen-ion concentration, the activation energy can also be expected to vary a little; but because of the uncertainty in formulating a detailed reaction mechanism on the basis of which such data could be interpreted quantitatively, no further determinations have been made.

(f) *Effect of Added Cupric Ions.*—Trial experiments showed that the colorimetric estimation of ferric iron in the presence of large amounts of ferrous iron with the " ferron " reagent was no longer reliable when cupric ions were present in the solution: abnormally high values were obtained. The effect of cupric ions on the oxidation of ferrous ions was therefore studied at oxygen pressures of about 100 atm., and the progress of the oxidation followed by permanganate titration as described on p. 4359. A series of experiments were carried out with various concentrations of cupric perchlorate in 0·51M-perchloric acid. The data were plotted as for a bimolecular reaction, an example being given in Fig. 2*b*. Although the addition of cupric ions increases the rate somewhat, the order of the reaction with respect to ferrous ion remains the same. Velocity constants were calculated from the slopes of the lines and the mean oxygen pressures obtaining throughout the experiments as described in Section (b).

A plot of these values of $k_{\text{exp.}}$ against the cupric-ion concentration is given in Fig. 7. It being assumed that $k_{\text{exp.}}$ shows the same variation with ionic strength as is found in the uncatalysed reaction, these values were adjusted to correspond to the lowest ionic strength obtained in the series, *i.e.*, 1·1, by interpolation from the data in Table 1 (Fig. 4). The broken curve in Fig. 7 passes through these corrected values. It appears that cupric ion is only a poor catalyst : its effect reaches a maximum with a 2·5-fold increase in $k_{\text{exp.}}$ when the relatively high concentration of 0·15—0·20M-Cu^{2+} is reached.

DISCUSSION

(i) *Comparison with Other Results.*—The results of the present study, obtained over a far wider range of experimental conditions than those of earlier investigations, confirm that the oxidation of ferrous ions by molecular oxygen is of first order with respect to oxygen and of second order with respect to ferrous ion. However, there are quantitative differences between oxidation in perchloric acid and in sulphuric acid as shown by Lamb and Elder (*loc. cit.*). In Table 2 their values for $k_{\text{exp.}}$ at 30° with different normalities of sulphuric acid are compared with values appropriate to perchloric acid, obtained by interpolation from the data at 25° plotted in Fig. 5, the temperature coefficient 1·65, calculated from Fig. 6, being used to allow for the 5° difference. A sharp rise in the magnitude of $k_{\text{exp.}}$ is to be noted for sulphuric acid at the lowest normality, but not for perchloric acid; with this exception the values of $k_{\text{exp.}}$ are roughly similar. More marked differences are found when cupric ion is present. The maximum increase in $k_{\text{exp.}}$ in perchloric acid is somewhat less than three-fold (Fig. 7), whereas Lamb and Elder found that $k_{\text{exp.}}$ increased more than 30 times, from $2{\cdot}87 \times 10^{-3}$ to 87 and 98×10^{-3} l. mole^{-1} atm^{-1}. hr.$^{-1}$ with 0·05 and 0·1M-cupric ion. This behaviour could be attributed to the ability of $SO_4^{=}$ and HSO_4^{-} ions to form ion-pair complexes, particularly in the cupric-ion catalysed reaction, where the cuprous ion is a likely intermediate.

TABLE 2. *A comparison of the velocity constants for the oxidation of ferrous ion by oxygen in sulphuric acid solutions at* 30° (*Lamb and Elder,* loc. cit.) *with those for oxidation in perchloric acid solution at* 30° *calculated from the present data.*

Acid normality	1·0	0·46	0·11	0·024	0·016
$10^3\,k_{\text{exp.}}$, l. mole^{-1} atm.$^{-1}$ hr.$^{-1}$ in H_2SO_4	2·87	2·86	4·15	5·54	12·65
$10^3\,k_{\text{exp.}}$, l. mole^{-1} atm.$^{-1}$ hr.$^{-1}$ in $HClO_4$	3·5	2·3	3·0	4·2	4·5

The experiments in section (a) at high oxygen pressures show convincingly that the oxidation studied is not a complicated coupled oxidation involving traces of organic impurities, because the reaction order remains substantially the same whilst a concentration of 0·13M-ferrous ion of a total concentration of 0·23M is oxidised. The identical kinetics and good quantitative agreement between velocity constants at high and low oxygen pressures are strong evidence that the oxidation under these more readily available conditions is also a true oxidation of the ferrous ion as such.

It is more difficult, however, to decide whether the results are the consequence of heavy-metal catalysis by trace impurities. The following considerations suggest that it is unlikely. First, good reproducibility was obtained with different preparations of the stock ferrous perchlorate solution. This involved a precipitation, and variations in the degree of adsorption of catalytic impurities might be expected which would have led to irreproducible oxidation rates. Irreproducible rates are in fact found in the uncatalysed oxidation of vanadic (V^{3+}) ions by oxygen, owing to the susceptibility of this oxidation to cupric-ion catalysis (Ramsey, Sugimoto, and De Vorkin, *J. Amer. Chem. Soc.*, 1941, **63**, 3480). Furthermore, there is a marked change in the kinetics of the vanadic-ion oxidation when it becomes catalysed. With a cupric-ion concentration of less than 10^{-6}M, the rate equation is $-\mathrm{d}[V^{3+}]/\mathrm{d}t = k_{\text{uncat.}}[V^{3+}][O_2]/[H^+]$, whereas the cupric-ion-catalysed rate, whilst still proportional to $[V^{3+}]/[H^+]$, is independent of oxygen pressure. The explanation suggested is that in the uncatalysed reaction the rate-determining step is

$$VOH^{2+} + O_2 \longrightarrow VO^{2+} + \text{etc.} \quad . \; . \; . \; . \; . \; . \; . \quad (a)$$

whereas with the cupric-ion concentration above a certain threshold value the following reaction, which does not involve oxygen, is more important

$$VOH^{2+} + Cu^{2+} \longrightarrow VO^{2+} + Cu^{+} + H^{+} \quad . \; . \; . \; . \quad (b)$$

In contrast to these reactions, the dependence of the ferrous-ion oxidation upon oxygen pressure, and the already high reaction order, suggest that it is not a catalytic process.

(ii) *Reaction Mechanisms, and Correlation with Data on the Decomposition of Hydrogen Peroxide.*—The second-order dependence on ferrous-ion concentration, fully borne out in the present study, shows that under these conditions the oxidation does not proceed by the simple sequence of electron transfer and radical reactions, giving rate equation (1), which were proposed by Weiss (*loc. cit.*). The uncatalysed oxidation of vanadic ions (p. 4354) is, however, in accord with this type of mechanism.

The increase in rate of the ferrous-ion oxidation when cupric ions are present is also contrary to the radical mechanism, unless additional reactions are brought in. For in the hydrogen peroxide system, cupric ions have been shown to increase the peroxide decomposition rate in a manner consistent with the cupric ion reacting some 25 times more rapidly than the ferric ion with O_2^-. A catalysis of the reaction between Fe^{3+} and O_2^- thus results through the two steps

$$Cu^{2+} + O_2^- \longrightarrow Cu^{+} + O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (c)$$

$$Cu^{+} + Fe^{3+} \longrightarrow Cu^{2+} + Fe^{2+} \quad . \; . \; . \; . \; . \; . \; . \quad (d)$$

(Barb, Baxendale, George, and Hargrave, *Trans. Faraday Soc.*, 1951, **47**, 462, 591). If (*c*) and (*d*) were the only reactions of copper ions in the oxidation reaction, then according to the radical mechanism a decrease in rate, and not an increase, should be observed. The reverse of reactions (*c*) and (*d*) could be considered to account for the increased rate of reaction, the mechanism of which need not necessarily have steps in common with the uncatalysed reaction. Reaction (*d*) would have to be rapid, and reaction (*c*) many times faster than the corresponding reaction between Fe^{2+} and O_2. Ramsey, Sugimoto, and De Vorkin (*loc. cit.*) have, in effect, suggested a similar mechanism for the cupric-ion catalysed vanadic-ion oxidation [reaction (*b*)].

A very straightforward mechanism for the uncatalysed oxidation ot ferrous ion involves the primary formation, in a rapidly established equilibrium (*e*), of a ferrous ion–oxygen complex which then reacts with a second ferrous ion in a rate-determining step (*f*) :

$$Fe^{2+} + O_2 \overset{k_e}{\rightleftharpoons} Fe^{2+}O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (e)$$

$$Fe^{2+}O_2 + Fe^{2+} + 2H^+ \xrightarrow{k_f} 2Fe^{3+} + H_2O_2 \quad . \; . \; . \; . \; . \; . \; . \quad (f)$$

Two more ferrous ions reacting with the peroxide molecule complete the reduction of oxygen to water : $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$. This mechanism accounts for the kinetics given by equation (2), but leaves unexplained the observation that $k_{\text{exp.}}$ is almost independent of $[H^+]$ and not proportional to $[H^+]^2$ as reaction (*f*) would imply. This difficulty can be resolved by introducing the two hydrogen ions in equilibria following reaction (*f*), so that in (*f*) itself ionised species are produced. One possibility is reaction (*g*) giving the ion-pair complexes $FeOH^{2+}$ and FeO_2H^{2+} whose existence was established by Evans, George, and Uri (*Trans. Faraday Soc.*, 1949, **45**, 230). Reaction (*g*) accounts

$$Fe^{2+}O_2 + H_2O,Fe^{2+} \underset{k_g'}{\overset{k_g}{\rightleftharpoons}} FeO_2H^{2+} + HOFe^{2+} \quad . \; . \; . \quad (g, g')$$

for the relative independence of $k_{\text{exp.}}$ with respect to $[H^+]$, and has the great merit of replacing (*f*), which has four reacting species, by a simple bimolecular reaction which can be envisaged as hydrogen-atom transfer between a water molecule of the solvation shell of one ferrous ion and the ferrous ion–oxygen complex. The small effect of $[H^+]$ on $k_{\text{exp.}}$ can be considered to arise through an ionisation of one of the water molecules which solvate the complex. But before considering this mechanism further, it is desirable to correlate the oxidation data with the peroxide decomposition data, particularly with regard to suggested reaction mechanisms, because a simple radical mechanism for the peroxide decomposition has also been found to break down under certain experimental conditions.

In the ferric-ion-catalysed peroxide decomposition, Barb, Baxendale, George, and Hargrave (*loc. cit.*) showed that the radical mechanism (*i*) accounts satisfactorily for the

$$\left.\begin{array}{ll}
\text{Initiation :} & Fe^{3+} + H_2O_2 \xrightarrow{k_i} Fe^{2+} + HO_2 + H^+ \\
\text{Propagation :} & Fe^{2+} + H_2O_2 \xrightarrow{k_o} Fe^{3+} + HO + OH^- \\
 & HO + H_2O_2 \xrightarrow{k_2} H_2O + HO_2 \\
 & Fe^{3+} + HO_2 \xrightarrow{k_4} Fe^{2+} + O_2 + H^+ \\
\text{Termination :} & Fe^{2+} + HO \xrightarrow{k_1} Fe^{3+} + OH^- \\
 & Fe^{2+} + HO_2 \xrightarrow{k_3} Fe^{3+} + O_2H^-
\end{array}\right\} \quad . \; . \; . \; . \; . \; . \quad (i)$$

observed kinetic behaviour, given by equation (3) at high values of the $[H_2O_2]/[Fe^{3+}]$ ratio :

$$-d[H_2O_2]/dt \propto [Fe^{3+}][H_2O_2]/[H^+] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

e.g., 50—1000, provided that termination by reaction of HO_2 predominates. This would be expected from data on the ferrous ion–peroxide system.

Stationary-state analysis of these reactions gives

$$-d[H_2O_2]/dt = 2(k_ik_ok_4/k_3)^{\frac{1}{2}}[Fe^{3+}][H_2O_2] \quad . \; . \; . \; . \; . \quad (4)$$

This mechanism thus accounts for the dependence on $[Fe^{3+}]$ and $[H_2O_2]$, and the correct $[H^+]$ dependence also follows if the steps with velocity constants k_i and k_4 are taken to proceed *via* the ionised species O_2H^- and O_2^-. However, with low ratios $[H_2O_2]/[Fe^{3+}]$ of about unity, rate equation (3) no longer holds, equation (5) taking its place :

$$-d[H_2O_2]/dt \propto [Fe^{3+}][H_2O_2]^{\frac{3}{2}}/[H^+]^{n \geqslant 1} \quad . \; . \; . \; . \; . \quad (5)$$

Although reference to the ferrous ion–peroxide system shows that termination by the HO radical should now predominate, this leads to the rate equation

$$-d[H_2O_2]/dt = 2(k_ik_ok_2/k_1)^{\frac{1}{2}}[Fe^{3+}]^{\frac{1}{2}}[H_2O_2]^{\frac{3}{2}} \quad . \; . \; . \; . \; . \quad (6)$$

with a hydrogen-ion dependence of $1/[H^+]^{\frac{1}{2}}$, derived from $(k_i)^{\frac{1}{2}}$. So there is a discrepancy with respect to the order of both $[Fe^{3+}]$ and $[H^+]$. Barb, Baxendale, George, and Hargrave considered as an additional initiation reaction (*h*) which, it will be seen, is another

$$Fe^{3+} + FeO_2H^{2+} \longrightarrow 2Fe^{2+} + O_2 + H^+ \quad . \; . \; . \; . \quad (h)$$

alternative for the reverse reaction of (*f*). Initiation by (*h*) gives the correct dependence on $[Fe^{3+}]$ if it replaces entirely initiation by (*i*), but this was contrary to the expected contribution of (*i*), as judged from the value of k_i obtained from experiments with high $[H_2O_2]/[Fe^{3+}]$. Furthermore, it left unexplained the $[H^+]$ dependence of (5), since both initiation reactions (*i*) and (*h*) are identical in this respect. It was therefore concluded that under these concentration conditions other reactions were present, which play no part either in the system at high values of $[H_2O_2]/[Fe^{3+}]$ or in the ferrous ion–peroxide system : and by inference reactions of the type (*h*) were to be neglected.

From experiments with isotopic oxygen, Cahill and Taube (*J. Amer. Chem. Soc.*, 1952, **74**, 2312) have put forward a different mechanism for both high and low ratios of $[H_2O_2]/[Fe^{3+}]$, in which two-equivalent oxidation of ferrous ion by peroxide also occurs, giving a Fe(IV) derivative which, by reacting with a further peroxide molecule, gives its own peroxide complex, FeO_2H^{3+}. Reactions of these intermediates provide part of a new chain propagation mechanism :

Initiation : $\mathrm{Fe^{3+} + H_2O_2 \rightleftharpoons FeO_2H^{2+} + H^+}$ . . . . K_{III}

$\mathrm{FeO_2H^{2+} \longrightarrow Fe^{2+} + HO_2}$ . . . . k_1

$\mathrm{Fe^{3+} + HO_2 \longrightarrow Fe^{2+} + O_2 + H^+}$

Propagation : $\mathrm{Fe^{2+} + H_2O_2 \longrightarrow Fe(IV) + 2OH^-}$ . . . . k_2

$\mathrm{Fe(IV) + H_2O_2 \longrightarrow FeO_2H^{3+} + H^+}$

$\mathrm{FeO_2H^{3+} \longrightarrow Fe^{3+} + HO_2}$

$\mathrm{Fe^{3+} + HO_2 \longrightarrow Fe^{2+} + O_2 + H^+}$

Termination : $\mathrm{Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO}$ . . . . . . k_4

$\mathrm{Fe^{2+} + HO \longrightarrow Fe^{3+} + OH^-}$

This mechanism accounts for rate equation (3) at high values of $[H_2O_2]/[Fe^{3+}]$, and, with alternative termination reactions governed by this ratio, it accounts for equation (5) too : however, the detailed agreement with data for the ferrous ion–peroxide system was not explored.

Now the following calculation, based on the present oxidation results, suggests that an additional initiation reaction involving two ferric ions and the peroxide molecule must necessarily be considered as well as other modifications to the radical reaction scheme, like those proposed by Cahill and Taube (*loc. cit.*). In view of the relative independence of $k_{\text{exp.}}$ with respect to $[H^+]$, only equations like (g') need examining, and (g') itself provides a good example since the detailed mechanism of the reverse reaction (*g*) is a very appropriate oxidation step. The two steps (*e*) and (*g*), together with the equilibria for the formation of the ion-pair complexes $FeOH^{2+}$ and FeO_2H^{2+}, constitute the reduction of oxygen to hydrogen peroxide by Fe^{2+} :

$$\mathrm{2Fe^{2+} + O_2 + 2H^+ \overset{K_j}{\rightleftharpoons} 2Fe^{3+} + H_2O_2} \quad . \ . \ . \ . \ . \ . \quad (j)$$

If $K_1 = [Fe^{3+}]/[FeOH^{2+}][H^+]$ and $K_2 = [Fe^{3+}][H_2O_2]/[FeO_2H^{2+}][H^+]$, then by combining the various equilibria, K_j is found to be $K_ek_g/K_1K_2k_g'$. A value of $K_j = 10^{-2}$ mole l.$^{-1}$ atm.$^{-1}$ at unit hydrogen-ion concentration and 25° can be calculated from the oxidation–reduction potentials of 0·682 v for the O_2–H_2O_2 couple (Latimer, " Oxidation Potentials," 2nd Edn., Prentice-Hall Inc., New York, 1952) and 0·741 v for the Fe^{3+}–Fe^{2+} couple at the appropriate ionic strength of 1·0 (Schumb, Sherrill, and Sweetser, *J. Amer. Chem. Soc.*, 1937, **59**, 2360). K_ek_g will be one half of $k_{\text{exp.}}$ determined in the oxidation experiments, since four ferrous ions, rather than two, are consumed per oxygen molecule when water is the final reduction product rather than peroxide. At unit hydrogen-ion concentration and 25°, K_ek_g thus has the value $2{\cdot}9 \times 10^{-7}$ l. mole^{-1} atm.$^{-1}$ sec.$^{-1}$, and hence $K_1K_2k_g' = 2{\cdot}9 \times 10^{-5}$ l.^{2} mole^{-2} sec.$^{-1}$. The hydrogen-ion dependence, which is implicit in the back reaction of (*j*) if it proceeds *via* the reaction path (g'), entails that $K_1K_2k_g'$ is given in general by $2{\cdot}9 \times 10^{-5}/[H^+]^2$ l.^{2} mole^{-2} sec.$^{-1}$ at the hydrogen-ion concentration usually employed.

According to the radical mechanism, $k_i = 9{\cdot}1 \times 10^{-7}/[H^+]$ l. mole^{-1} sec.$^{-1}$ at 25°, calculated from data for high $[H_2O_2]/[Fe^{3+}]$ values, hence by equating the initiation rates, it follows that (g') should predominate at $[Fe^{3+}] > 9{\cdot}1 \times 10^{-7}.[H^+]/(2{\cdot}9 \times 10^{-5}) =$

0·031[H$^+$]. The ferric-ion and hydrogen-ion concentrations used have therefore been such that (*g'*) should play an important rôle, *e.g.*, high values of [H_2O_2]/[Fe^{3+}], 1—20 × 10^{-3}M-Fe^{3+} and 5—200 × 10^{-3}N-H^+ : low values of [H_2O_2]/[Fe^{+3}], 5 × 10^{-2}M-Fe^{3+} and 2·8—25 × 10^{-2}N-H^+.

Although the initiation rate constant, given by k_1K_{III}, has not been evaluated for the mechanism proposed by Cahill and Taube (*loc. cit.*), provided that the chain length given by k_2/k_4 has values greater than 10^2—10^3, then k_1K_{III} would be less than 1·2 × 10^{-5}—1·2 × 10^{-6} because the overall decomposition constant, given by $k_1K_{\text{III}}k_2/k_4$, has the value 1·2 × 10^{-3} l. mole^{-1} sec.$^{-1}$ at unit hydrogen-ion concentration and 25° (Barb, Baxendale, George, and Hargrave, *loc. cit.*). In these circumstances, therefore, reaction (*g'*) should also play an important rôle in Cahill and Taube's mechanism. In spite of the uncertainties inherent in these calculations, it does appear that the contribution of an additional initiation reaction of the type described warrants consideration in the peroxide decomposition mechanism.

Returning to a consideration of the oxidation, we see that Weiss's revised mechanism (*Experientia*, 1953, **9**, 61) is in many respects similar to that developed above, except that he proposed an ion-pair structure for the complex, $Fe^{3+}O_2^-$, and did not consider the second step in detail. On the basis of heats and entropies of reaction, $Fe^{3+}O_2^-$ appears to be a less favoured structure than $Fe^{2+}O_2$, where electron transfer within the complex has not occurred. If we take ($E_{O_2} + S_{O_2^-}$) = 79 kcal./mole, S_{O_2} = 3 kcal./mole, and $I_{Fe^{2+},aq.}$ = 95 kcal./mole, we see that the reaction $Fe^{2+}{}_{aq.} + O_2 \longrightarrow Fe^{3+}{}_{aq.} + O_2^-$ is endothermic to the extent of about 19 kcal./mole. $\Delta H°$ values for the formation of ion-pair complexes of the ferric-ion range from −4·3 to +8·5 kcal./mole as shown in Table 3;

TABLE 3. ΔH° *for the formation of ion-pair complexes of ferric ion.*

Complex	$FeOH^{2+}$	FeO_2H^{2+}	FeF^{2+}	$FeCl^{2+}$	$FeBr^{2+}$	FeN_3^{2+}
$\Delta H°$ (kcal./mole)	−1·2	+1·8	+7·5	+8·5	+6·1	−4·3

(For references see Uri, *Chem. Reviews*, 1952, **50**, 375, Table 10).

and the value for $Fe^{3+}O_2H^-$, which on structural considerations should be the best approximation to $Fe^{3+}O_2^-$, is 1·8 kcal./mole. Thus the reaction between the ferrous ion and oxygen giving a complex $Fe^{3+}O_2^-$ should, according to these values, be endothermic to about 21 kcal./mole. The entropy change accompanying the reaction $Fe^{2+} + O_2 \longrightarrow Fe^{3+}O_2^-$ should also be less favourable than that accompanying complex-formation without charge transfer, because the greater charge separation in $Fe^{3+}O_2^-$ would involve tighter bonding of the water molecules in the solvation shell. It is noteworthy that kinetic studies of the analogous oxidation of myoglobin, a ferrous hæmoprotein ($MbFe^{2+},H_2O$), which readily combines reversibly with oxygen to give a covalently bonded complex MbFe(II)O_2^{2+}, have led to a provisional value of about 20 kcal./mole for the energy required to excite MbFe(II)O_2^{2+} to $MbFe^{3+},O_2^-$ (George and Stratmann, *Biochem. J.*, 1954, **57**, 568).

In conclusion, one aspect of the ferrous-ion oxidation can profitably be compared with those of similar oxidation–reduction reactions. The simple radical mechanism (Weiss, *loc. cit.*), if it occurred, would consist of a very endothermic step, −19 kcal./mole, followed by a very exothermic step, +19—29 kcal./mole (Barb, Baxendale, George, and Hargrave, *loc. cit.*). The more complicated reaction path suggested above utilises the heat available from the latter reaction, which would otherwise be dissipated, to " drive " the former reaction, by resorting to the transfer of two oxidation equivalents at the same time—one intermolecularly and the other intramolecularly, as shown in (*g*).

Similar thermochemical relations also hold for the two radical reactions long believed to account for the oxidation of the ferrous ion by hydrogen peroxide :

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO + OH^- - 5 \text{ kcal./mole} \quad . \quad . \quad . \quad (l)$$

$$Fe^{2+} + HO \longrightarrow Fe^{3+} + OH^- + 44 \text{ kcal./mole}$$

and Cahill and Taube's suggestion that Fe(IV) is formed initially, $Fe^{2+} + H_2O_2 \longrightarrow$ Fe(IV) + $2OH^-$, could be considered as another example of a two-equivalent oxidation, more favoured because of such energy relations. Indirect support for this kind of reaction mechanism comes from the peroxide reaction of metmyoglobin, $MbFe^{3+},H_2O$, the ferric form of myoglobin, which appears to follow a similar path to this with all the iron compounds one oxidation number higher. The only relatively stable intermediate is the single-equivalent oxidation product, MbFe(IV). Yet calculations of its heat of formation suggest that it is not formed in a reaction corresponding to (*l*), but by the single-equivalent reduction of a two-equivalent oxidation product formed initially. This is in effect a quinquevalent iron compound, and may be the myoglobin analogue of the first intermediate compound appearing in peroxidase and catalase reactions (George and Irvine, *Biochem. J.*, 1952, **52**, 511; Chem. Soc. Special Publ. No. 1, 1954, " Kinetics and Mechanism of Inorganic Reactions in Solution," London, 1954).

EXPERIMENTAL

" AnalaR " grade reagents were used wherever possible. 0·24M-Stock solutions of ferrous perchlorate and cupric perchlorate were prepared by carefully mixing solutions containing equivalent amounts of the sulphate and barium perchlorate, allowing the precipitate to settle, decanting, and filtering. A little perchloric acid was added to the ferrous sulphate before precipitation, making the solution 5×10^{-3}N; it was kept in a refrigerator at 4°. Analysis showed that the ferric-ion concentration initially present in such a stock solution varied from about 1×10^{-4} to 3×10^{-4}M.

The kinetics of ferrous-ion autoxidation in perchloric acid solution at 25—40° were studied by two methods. In the first, air or oxygen at atmospheric pressure was bubbled through solutions of ferrous perchlorate made up in various concentrations of perchloric acid and kept in a thermostat. The extent of oxidation was determined by colorimetric estimation of the ferric ion produced by means of " ferron," 8-hydroxy-7-iodoquinoline-5-sulphonic acid, based on that suggested by Swank and Mellon (*Ind. Eng. Chem. Anal.*, 1937, **9**, 406).. A 2, 5, or 10 ml. sample of the reaction mixture, or a suitably diluted portion of it depending on the expected ferric-iron concentration, was added to 25 ml. of a buffer made from 50 ml. of 0·5M-sodium chloroacetate and 200 ml. of 0·5M-chloroacetic acid diluted to 1 l. 2 Ml. of a 2% solution of the ferron reagent in water were then added, followed by distilled water to give a final volume of 100 ml. The optical density of the resulting greenish-blue solution was measured in a 4-cm. cell by means of a Hilger Spekker colorimeter equipped with Ilford 607 orange filters and Chance's protective heat-absorbing glass. A linear calibration curve was obtained with ferric nitrate solution as standard, an optical density of 0·50 corresponding to 4×10^{-5}M-ferric iron in the final solution. Control calibrations showed that 10^{-2}M-ferrous iron in the solution had no effect. Since this concentration is at least twice that present in samples made up from portions of the reacting mixture during oxidation experiments, this method of analysis is well suited for following the progress of the oxidation.

In the second method similar solutions of ferrous perchlorate were placed in a small cylindrical glass vessel which fitted snugly inside a hollow steel block connected to an oxygen cylinder. The block had the dimensions 5 × 5 × 15 cm. and was made in two pieces which screwed together. It was drilled to a depth of 10·5 cm., and in this cavity, of diameter 2 cm., was placed the reaction vessel, a glass cylinder of 1·7 cm. internal diameter with flattened, drawn-off ends. The ferrous perchlorate solution, 9 ml. in all, was introduced through a hole 4·5 cm. from one end of the cylindrical vessel. This hole was not closed during a run to ensure that at all times the solution was in contact with the oxygen at high pressure. A few glass beads placed in the vessel, with a tilting mechanism operating at 3½ cycles/min., stirred the solution effectively without splashing it. The progress of oxidation was followed by titrating 1 ml. portions with potassium permanganate.

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