

THE RATE CONSTANT OF THE REACTION BETWEEN FERROUS IONS AND HYDROGEN PEROXIDE IN ACID SOLUTION¹

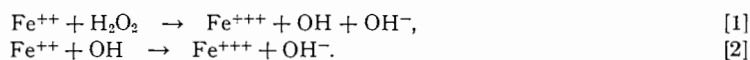
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ABSTRACT

Identical values of the bimolecular rate constant of the ferrous ion-hydrogen peroxide reaction were obtained from intercomparisons of the methods previously used in following this reaction. In perchloric acid the bimolecular rate constant is unaffected by acid concentration; in sulphuric acid it increases slightly in acid concentrations above 10^{-2} *N*. The results agree with and explain the differences between those obtained by Baxendale and by Dainton, but are only in marginal agreement with those recently reported by Weiss.

INTRODUCTION

In acid solution ferrous ions react with hydrogen peroxide in a two step process:



All side reactions are eliminated if the equivalent concentration of hydrogen peroxide is less than that of ferrous ion and if the solutions are free from organic contaminants (1). Reaction [2] is rapid; reaction [1] is the rate-controlling step. Under these conditions the reaction is second order. The rate of disappearance of hydrogen peroxide is equal to one half the rate of ferric ion production:

$$[A] \quad -d[\text{H}_2\text{O}_2]/dt = \frac{1}{2}d[\text{Fe}^{+++}]/dt = k_0[\text{Fe}^{++}][\text{H}_2\text{O}_2].$$

In the integrated form this equation becomes

$$[B] \quad k_0 t = [2.303/(a-2b)] \log [2b(a-x)/\{a(2b-x)\}],$$

where

- a* is the initial concentration of ferrous ion,
- b* is the initial concentration of hydrogen peroxide,
- x* is the concentration of ferric ion produced in time *t*,
- k*₀ is the bimolecular rate constant.

Experimental values of *k*₀ obtained in various investigations differ considerably, and some disagreement exists as to the value of the activation energy. A summary of published values is given in Table I; comments on these experiments are made below.

Haber and Weiss (5) used large volumes of solution (~2 liters) and quenched the reaction by the addition of acid permanganate. The extent of the reaction was calculated from the amount of permanganate reduced. At the reactant concentrations used ($[\text{Fe}^{++}] = 3 \times 10^{-3}$ *M*, $[\text{H}_2\text{O}_2] = 5 \times 10^{-4}$ *M*) the reaction time before quenching was usually about fourteen seconds, at which time about one half of the hydrogen peroxide had disappeared. Since complete mixing of volumes of this magnitude requires several seconds, it is likely that there is considerable error in estimating the reaction time.

Baxendale, Evans, and Park (2) followed the reaction by measuring the disappearance of ferrous ion. At a given time the reaction was quenched by the addition of a solution

¹Manuscript received December 3, 1956.

Contribution from the Research Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 427.

TABLE I
 PUBLISHED RESULTS ON THE KINETICS OF THE FERROUS ION - HYDROGEN PEROXIDE REACTION

Authors	Method	E (cal.)	$k_0(20^\circ \text{C.})$	Temperature range studied, $^\circ \text{C.}$	A (pre- exponential term)	Medium
Haber and Weiss (1934)	Quenching with KMnO_4	8500 ± 500	23	6-45	4×10^7	Unknown but "acidified"
Baxendale, Evans, and Park (1946)	Quenching with $\alpha\alpha'$ -dipyridyl in acetate buffer	10,100	52	12-35	7.78×10^9	1 N sulphuric acid
Barb, Baxendale, Hargreave, and George (1951)	Quenching as in Ref. 2	9,400	43.4	0-25	4.45×10^9	Perchloric acid 0.0025 N - 0.5 N; sulphuric acid 0.0025 N
Rigg, Taylor, and Weiss (1954)	Followed production of Fe^{+++} optically	8,460	51.4	15-41	1.05×10^8	0.5-0.8 N sulphuric acid
Dainton and Sutton (1953)	Quenching with: (1) <i>o</i> -phenanthroline plus buffer and (2) ceric ion	Miscellaneous experiments { $k_0(18^\circ \text{C.}) = 42$ $k_0(25^\circ \text{C.}) = 65$				0.8 N sulphuric acid

containing acetate buffer, $\alpha\alpha'$ -dipyridyl, and fluoride ion. The ferrous ion was chelated by the $\alpha\alpha'$ -dipyridyl at pH 4-7, forming a stable complex whose color is suitably intense for colorimetric analysis, while the fluoride ion formed a complex with the ferric ion, inhibiting the slow reduction of ferric ion by hydrogen peroxide.

Barb *et al.* (1) repeated this work later (1951) using the same experimental technique, but covering a much wider range of acid and reactant concentrations. The value of the bimolecular rate constant at 20° C. was found to be about 20% lower in the later work. Baxendale explained this by remarking that the importance of the complete exclusion of organic materials was not fully appreciated in his early work. Since rigorous purification procedures were used in the 1951 experiments more confidence was put in the later value.

Dainton and Sutton (4) measured k_0 in 0.8 *N* sulphuric acid. They followed the reaction (a) by measuring the ferrous concentration after quenching with acetate buffer and *o*-phenanthroline (cf. $\alpha\alpha'$ -dipyridyl) and (b) by adding excess ceric ion which oxidized both ferrous ion and hydrogen peroxide. In the latter case, the amount of ferric ion produced may be calculated from the measured decrease in ceric ion concentration. Within experimental error the same value of k_0 was obtained by both methods. This value agrees with Baxendale's 1946 value.

Taylor and Weiss (8) and Rigg, Taylor, and Weiss (6, 7) carried out the reaction in a spectrophotometer cell, maintained at constant temperature, and measured directly the ferric ion produced. As these authors point out (6, 7, 8) this method of following the reaction should give the most reliable results. The results in reference (8) were later (6, 7) found to be in error. The value of k_0 found by Rigg, Taylor, and Weiss at 20° C. agrees with that found by Baxendale (2); however, the activation energy observed (8640 cal.) was somewhat lower than that reported by Baxendale (2).

Throughout these experiments it had been accepted that the type or concentration of acid (sulphuric or perchloric) has no effect on the value k_0 or the activation energy. There is in fact only limited experimental support for this view (2, 7). While no effect of acid concentration has been found in perchloric acid solutions (2), a systematic study of the effect of acid concentration has not been made in sulphuric acid solutions.

From the evidence presented in the above papers, there seems to be no reason why the various methods of following the reaction should give different values of the bimolecular rate constant. In an attempt to resolve these discrepancies, the reaction of ferrous ion with hydrogen peroxide in acid solution has been investigated along the following lines.

1. An intercomparison of the various methods of following the reaction has been made, using the same initial ferrous ion and hydrogen peroxide solutions.
2. Values of the bimolecular rate constant k_0 were measured as a function of temperature and acid concentration in both sulphuric acid and perchloric acid. The reaction was followed by the method considered most suitable from the results of the first series of experiments.

EXPERIMENTAL

Three methods of following the reaction have been investigated—quenching by chelation, quenching with ceric ion, and direct optical observation of the rate of ferric ion formation. These are described in detail below with suitable comment on the technique.

The reaction vessel, shown in Fig. 1, was carefully cleaned and dried. A 20 ml. volume of ferrous ion solution was pipetted into the smaller compartment, while 25 ml. of

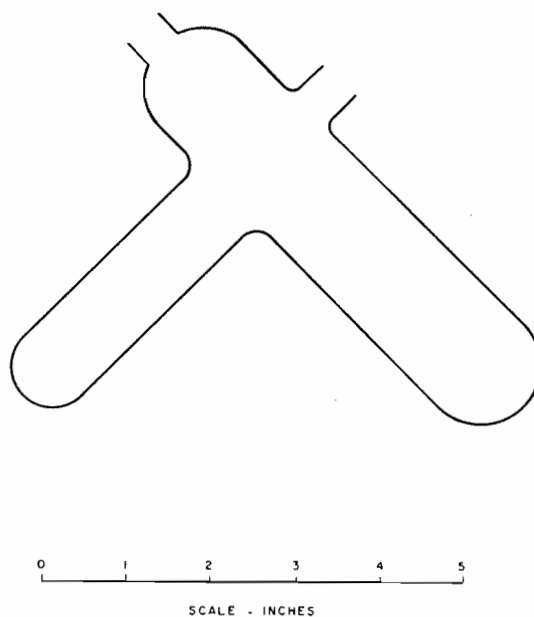


FIG. 1. Mixing vessel.

hydrogen peroxide solution was pipetted into the other. The vessel was placed in a constant temperature water bath and allowed to come to temperature. The reactants were mixed by rapidly pouring the solution from one compartment to the other.

Methods of Following the Reaction

I. Quenching by Chelation

The quenching solution contained 3 *M* ammonium acetate, 0.2 *M* ammonium fluoride, and sufficient *o*-phenanthroline to chelate all the ferrous ion. Ammonia was present in sufficient amount to neutralize approximately the acid in the reacting solution.

To stop the reaction, 5 ml. of the quenching solution was added to the reacting solution from a plunger pipette. This method has the advantage that the resultant solution is suitably colored (ferrous *o*-phenanthroline complex) for colorimetric analysis.

The amount of ferrous ion present was determined by measuring the light absorption of the solution at 510 $m\mu$ in a Beckman Spectrophotometer. The extinction coefficient for the complex was determined in separate experiments and was found to be 11,250. Although this value is 1% higher than the accepted value of 11,110 (3), the same result was obtained repeatedly using different sources of two primary standards, viz., ferrous ammonium sulphate and potassium dichromate.

Normally optical measurements were made using 1 cm. cells, but where necessary, cells of longer path length were used. This was the case for reactions in 1 *N* perchloric acid, where it was found that the ferrous *o*-phenanthroline color faded on standing in strong perchlorate ion solutions. In this particular case, the 50 ml. of solution was diluted with water to 500 ml. (where the color was stable) and optical measurements were made with 10 cm. cells.

The initial ferrous ion concentration was measured against a blank consisting of the acid plus the buffer. For other solutions, a method of differential spectrophotometry was used. Here the quenched *reacting* solution was used as a "blank" and the "quenched" *initial* solution (ferrous ion plus 25 ml. of appropriate acid) used as the "unknown".

In this way a direct measure of the ferrous ion disappearance, i.e., ferric ion production, was made. The initial amount of hydrogen peroxide was measured by allowing the reaction to go to completion before "quenching". Its concentration is equal to one-half of the total ferrous ion disappearance. In all cases initial ferrous ion and hydrogen peroxide determinations were made in triplicate. Suitable arithmetical corrections were made to relate the measured concentration of ferrous ion to that in the reacting solution.

II. Quenching with Ceric Ion

The quenching solution was ceric ion in 1 *N* sulphuric acid. The ceric ion concentration was such that 1 ml. of solution gave a 5% stoichiometric excess of ceric ion over the initial ferrous ion plus hydrogen peroxide. After quenching, 20 ml. of the original ferrous ion was added to reduce the ceric ion and give an excess of ferrous ion. A 5 ml. volume of the buffer solution described in method I was added, and the concentration of ferrous *o*-phenanthroline complex measured spectrophotometrically as before. The difference between the ferrous ion concentration of the reacting solution and the initial solution after similar treatment for analysis was measured directly. Suitable arithmetical corrections were made for the dilution. The amount of ferric ion produced in this system is equal to one-half the difference in ferrous ion concentration. Initial concentrations of hydrogen peroxide and ferrous ion were determined by method I.

III. Direct Measurement of the Ferric Ion Concentration

(a) *In sulphuric acid.*—The temperature of a spectrophotometer cell compartment was controlled to $\pm 0.05^\circ\text{C}$. by circulating water. The reactant solutions were brought to this temperature, mixed, and poured into a 1 cm. optical cell. The absorption of light at $320\text{ m}\mu$ was measured at 30 second intervals for about five minutes. At this wavelength, light absorption is entirely due to ferric ion. The initial concentrations of hydrogen peroxide and ferrous ion were determined by method I. The extinction coefficient of ferric ion under the experimental conditions was found by allowing the reaction to go to completion (t_∞). This extinction coefficient is equal to the optical density at t_∞ divided by twice the initial hydrogen peroxide concentration.

(b) *In perchloric acid.*—The rate of ferric ion production in perchloric acid solutions was measured by a continuously recording ultraviolet spectrophotometer. No facility existed for thermostating solutions in the cell compartment, so several runs were made at the prevailing room temperature ($19\text{--}21^\circ\text{C}$.). The values of k_0 obtained were normalized to one temperature assuming $E = 9500\text{ cal}$.

Measurements were made at a wavelength of $235\text{ m}\mu$ where the light absorption is due to ferric ion only. Initial concentrations of hydrogen peroxide and ferrous ion were found by method I. The extinction coefficient of ferric ion was determined in the same manner as in method III-a.

Reagents

Perchloric acid: Merck Reagent perchloric acid was vacuum distilled at 100°C . The middle 60% was retained.

Sulphuric acid: Nichol's chemically pure sulphuric acid was used.

Hydrogen peroxide: Merck 30% Superoxol was suitably diluted with water or acid.

Ferrous ion solutions:

(a) in sulphate solutions: Reagent ferrous ammonium sulphate was dissolved in dilute sulphuric acid;

(b) in perchlorate solutions: Johnson, Matthey, Mallory spectrographically pure iron was dissolved in excess perchloric acid.

Water: All water, including that used for final rinsing of the apparatus, was distilled from alkaline permanganate.

Ceric ion solutions: Ceric ammonium sulphate was dissolved in 1 *N* sulphuric acid to give the desired ceric ion concentration.

o-Phenanthroline: G. Frederick Smith *o*-phenanthroline was dissolved in 95% ethanol and added to the quenching solution.

Ammonium acetate, ammonium fluoride, and ammonia were all reagent grade.

RESULTS

Comparison of the Methods

Preliminary experiments in sulphuric acid solution, using method III-*a*, confirmed that the reaction was first order with respect to both hydrogen peroxide and ferrous ion. For the remainder of the experiments the following initial concentrations were chosen: $[Fe^{++}] = 100\text{--}120 \mu\text{M./l.}$, $[H_2O_2] = 20\text{--}25 \mu\text{M./l.}$ With these initial concentrations the half-life of the reaction was about three minutes at room temperature.

In all cases a plot of $\log [2b(a-x)/\{a(2b-x)\}]$ vs. t gave a straight line passing through the origin. Usually six determinations were made for each such plot. The error in k_0 is estimated to be $\pm 2\%$, 1% for the determination of the slope of the second order plot, and 1% for the determination of the absolute value of $1/(a-2b)$.

Values of k_0 in 0.1 *N* perchloric acid and 0.8 *N* sulphuric acid were determined at 20.2° C. using all three methods of following the reaction. The same initial solutions were used for each acid medium ($[Fe^{++}] \cong 120 \mu\text{M./l.}$, $[H_2O_2] \cong 20 \mu\text{M./l.}$). The results are reported in Table II. There is no significant difference in the results obtained by the three methods.

TABLE II
VALUES OF k_0 DETERMINED BY THE THREE METHODS
 $T = 20.2^\circ \text{C.}$

	k_0 (l. mol. ⁻¹ sec. ⁻¹)	
	In 0.1 <i>N</i> HClO ₄	In 0.8 <i>N</i> H ₂ SO ₄
Method I	41.3	50.4
Method II	41.7	50.6
Method III- <i>a</i>		51.6
III- <i>b</i>	41.8, 40.7	

The choice of method of following the reaction will depend on the convenience of analysis and the accuracy required. Method I is generally the most convenient and accurate method provided the ferrous ion concentration is less than ten times that of hydrogen peroxide. Method II is capable of greatest sensitivity, and is recommended where the concentrations of both reactants are below 10^{-5} *M*. Method III is in principle the most widely applicable, since ferric ion is the only light-absorbing material under the conditions used. However, the extinction coefficient of ferric ion varies with the type of acid and its concentration and temperature, and in practice must be determined in separate experiments.

The Effect of Variables on the Bimolecular Rate Constant k_0

In the experiments reported below, method I was used.

The value of k_0 was determined for a series of acid concentrations over a range of temperature (0–40° C.) in both sulphuric acid and perchloric acid solutions. Activation energies were calculated from the usual plot of $\log k_0$ vs. $1/T$. The values of E and of k_0 at 20° C. are recorded in Table III. Additional experiments showed that the presence of chloride ion in millimolar concentrations had no effect on either the rate or the activation energy.

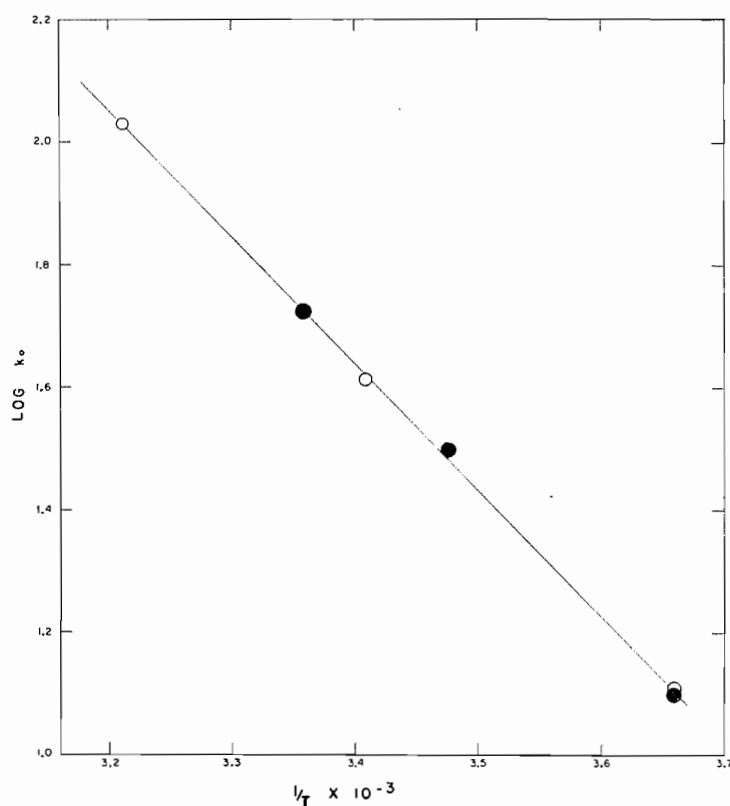


FIG. 2. Plot of $\log k_0$ vs. $1/T$ for the ferrous ion - hydrogen peroxide reaction in perchloric acid.
○ Present experiments ● Baxendale (1951)

In agreement with the results of Baxendale (2), we find that in perchloric acid solutions the rate is independent of the acid concentration above 10^{-3} M acid. At lower acid concentrations side reactions are probably present (2), and this may account for the higher value of both E and k_0 in 5.3×10^{-4} M acid. (See Table III.)

Assuming this independence of acid concentration, mean values of k_0 in perchloric acid solutions were calculated at each temperature. Fig. 2 is a plot of $\log k_0$ vs. $1/T$ for these data, together with the data reported by Baxendale. The two sets of data are clearly in close agreement, and in perchloric acid solutions the rate equation is

$$k_0 = 5.3 \times 10^8 e^{-9450/RT} \text{ l. mol.}^{-1} \text{ sec.}^{-1}.$$

TABLE III
VALUES OF E AND k_0 (20° C.) IN VARIOUS ACID MEDIA

Acid concentration, equiv./l.	E , cal.	$k_0(20^\circ \text{C.})$, l. mol. ⁻¹ sec. ⁻¹
In sulphuric acid		
0.80	9750	51.4
0.10	9650	49.3
0.0105	9850	42.6
0.0014	9850	42.6
Mean 9750		
In perchloric acid		
1.00	9450	44.6
0.10	9450	41.5
0.011	9400	42.3
0.00167	9600	42.6
0.00053	10330	55.0

$$k_0 \text{ (in HClO}_4\text{)} = 5.3 \times 10^8 e^{-9450/RT}$$

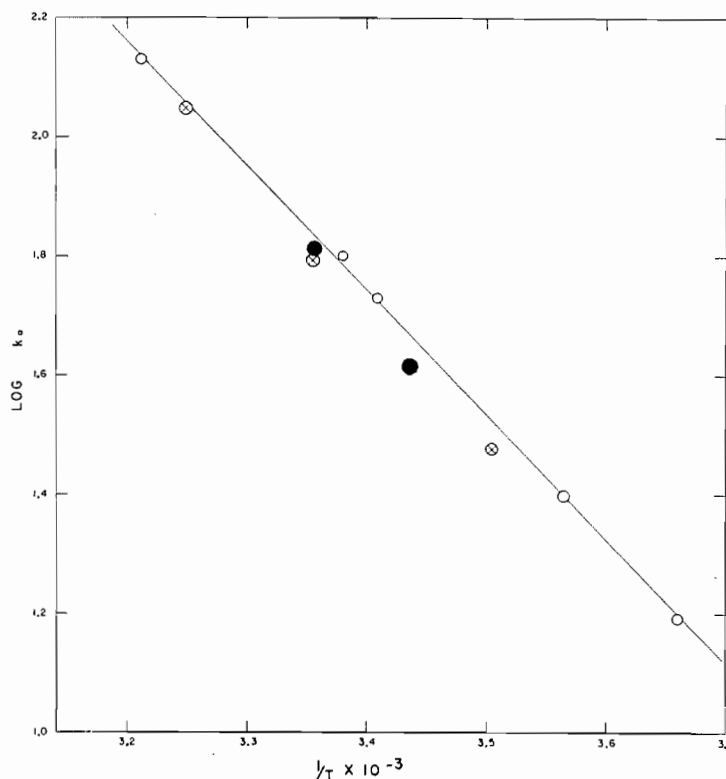


FIG. 3. Plot of $\log k_0$ vs. $1/T$ for the ferrous ion - hydrogen peroxide reaction in 0.8 N sulphuric acid.
 ○ Present experiments ⊗ Baxendale (1946) ● Dainton and Sutton (1953)

In sulphuric acid solutions the activation energy appears to be independent of the sulphuric acid concentration. The value of $k_0(20^\circ \text{C.})$ increases with acid concentration, and this is interpreted as an increase in the temperature independent factor. At present, we can offer no explanation for this behavior.

At low acid concentrations at room temperature $k_0(\text{H}_2\text{SO}_4)$ is fortuitously equal to $k_0(\text{HClO}_4)$, and this observation led Baxendale to assume the rate to be independent of the acid medium, and hence independent of sulphuric acid concentration. Fig. 3 shows a plot of $\log k_0$ vs. $1/T$ for 0.8 *N* sulphuric acid. We have included on this graph data from Dainton and Sutton (4) and also from Baxendale, Evans, and Park (2). Although the latter group used 1 *N* sulphuric acid as the medium, little change in k_0 is expected between 0.8 and 1.0 *N* sulphuric acid.

An examination of Fig. 3 shows that the results of previous workers and the present work are in reasonable agreement. Although previously obtained data lie below the straight line, this discrepancy is probably due to differences in analytical calibrations. This difference will not affect the slope of the line. Baxendale's results of 1946 are not anomalous, but are in agreement with values obtained in the same concentration of sulphuric acid. In 0.8 *N* sulphuric acid the rate expression is

$$k_0 = 9.6 \times 10^8 e^{-9750/RT} \text{ l. mol.}^{-1} \text{ sec.}^{-1}.$$

The rate expression in 0.5–0.8 *N* sulphuric acid reported by Weiss (6, 7) is $\bar{k}_0 = 1.05 \times 10^8 e^{-8460/RT} \text{ l. mol.}^{-1} \text{ sec.}^{-1}$. In the temperature range 15–25° C. the values of k_0 calculated from Weiss' rate expression agree within $\pm 4\%$ of the present work; at 40° C. there is a difference of 14%. These values result in differences in both the activation energy and the temperature independent factor.

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