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James G. Brummer
The University of Montana

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KINETICS AND MECHANISM OF THE OXIDATION
OF FERROUS-ION BY IODATE IN A STRONG
PERCHLORIC ACID MEDIUM

by

James Brummer

B.S., University of California at Davis, 1975

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ABSTRACT

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Kinetics and Mechanism of the Oxidation of Ferrous-Ion by Iodate in a Strong Perchloric Acid Medium

Director: Richard J. Field

The oxidation of Fe(II) by IO$_3^-$ in a strong perchloric acid medium proceeds according to the following overall stoichiometry:

$$10 \text{Fe(II)} + 21\text{IO}_3^- + 12\text{H}^+ \rightarrow 10\text{Fe(III)} + \text{I}_2 + 6\text{H}_2\text{O}$$

Our study was carried out at 30.0 ± 0.2°C and at an ionic strength of 1.5 M. The reaction is autocatalytic in the production of iodine. Experiments involving continuous extraction of iodine from the reaction medium into an inert carbon tetrachloride layer eliminated this autocatalysis. Under conditions in which autocatalysis is suppressed, the rate of oxidation (R) obeys the following expression:

$$R = 1.05 \pm 0.07 \times 10^{-3} \text{ M}^{-2} \text{ sec}^{-1} (\text{H}^+) (\text{Fe(II)}) (\text{IO}_3^-)$$

This rate law only holds for acid concentrations between .556 M and 1.44 M. Experiments were also performed for reaction systems in which product iodine was allowed to accumulate. These data are much more complex.

A mechanism is proposed to explain the experimental data. For experiments in which iodine is extracted from the reaction medium the rate limiting process is an electron transfer from Fe(II) to the species H$_2$I$^+$O$^-$ producing water, Fe(III), and IO$_2$. This step is preceded by successive protonations of IO$_3^-$ and is followed by a series of rapid one-electron oxidations of Fe(II) by oxyiodine intermediates (IO$_2$, HOIO, IO, HOI) leading to iodine. If iodine is not extracted from the reaction mixture, autocatalysis will be initiated through the hydrolysis equilibrium of iodine with iodide and hypoiiodous acid (HOI). The iodide so generated reacts rapidly with IO$_3^-$ producing iodous acid (HOIO) and more hypoiiodous acid. The HOI and HOIO then react with Fe(II) to produce iodine.

Numerical solution of the system of differential equations resulting from the proposed mechanism reproduced all experimental facts.
ACKNOWLEDGMENTS

I wish to extend my deepest appreciation to my advisor and friend Dr. Richard J. Field whose guidance, patience, and encouragement have been of great value in my graduate education.

I would also like to thank the National Science Foundation and the University of Montana for funding the work contained in this thesis.
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ABBREVIATIONS

A list of abbreviations used through this thesis is:

Fe(II), ferrous-ion; (Fe(II)), concentration of Fe(II); (Fe(II))₀, initial concentration of Fe(II); I⁰₃⁻, iodate-ion; (I⁰₃⁻), concentration of I⁰₃⁻; (I⁰₃⁻)₀, initial concentration of I⁰₃⁻; H⁺, hydrogen-ion; (H⁺), concentration of H⁺; (H⁺)₀, initial concentration of H⁺; I₂, iodine; (I₂), I₂ concentration; (I₂)₀, initial I₂ concentration; ((I⁰₃⁻)/(Fe(II)))₀, initial ratio of (I⁰₃⁻) to (Fe(II)); HIO₃, iodic acid; IO₂, iodine dioxide radical; HOIO, iodosous acid; IO, iodine oxide radical; HOI, hypoiodous acid; I⁻, iodide-ion; °C, degrees celsius; Fe(III), ferric-ion; H₂O, water; HOOH, hydrogen peroxide; kcal, kilocalories; ClO₄⁻, perchlorate-ion; (ClO₄⁻), perchlorate-ion concentration; δ( )/δt, time derivative of ( ); k, rate constant; K, equilibrium constant; M, molarity; OH⁻, hydroxide-ion; sec, seconds; ml, milliliters; min, minutes; O₂, oxygen; aq, aqueous; g, gas; l, liquid; s, solid.
CHAPTER I

INTRODUCTION

A. STATEMENT OF PROBLEM AND PURPOSE

The oxidation of Fe(II) by IO$_3^-$ in strong perchloric acid media proceeds according to the stoichiometry of equation (1).

\[ 5 \text{Fe(II)} + \text{IO}_3^- + 6\text{H}^+ \rightarrow 5\text{Fe(III)} + \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O} \]

Perchlorate is the anion of choice in kinetic studies of inorganic solution phase reactions because of its kinetic inertness as well as its reluctance to complex with metallic cations. Reaction (1) proceeds rapidly to completion at 25°C, with a Gibbs Free Energy change of -51.0 Kcal. The reaction is autocatalytic in the production of iodine.

Little work has been devoted to the kinetic study of reaction (1) despite its potential as a source of information on oxyiodine chemistry. Mitzner, Fischer, and Leupold$^1$ recently investigated its kinetics and determined a rate law from which they proposed a mechanism for the reaction. For reasons to be outlined later in this account, their conclusions are likely to be erroneous. We therefore have embarked on a similar study. The goals of the present investigation are to determine
a rate law which describes the rate of reaction (1), derive a mechanism consistent with this rate law and all other experimental facts, and finally determine rate constants for elementary processes involving unstable oxyiodine compounds. In a more general sense, an understanding of the kinetics of process (1) will lead to a better understanding of other reaction systems involving oxyiodine compounds, especially the oscillating Bray-Liebhafsky Reaction.

B. LITERATURE SURVEY

Of the chemistry of oxyhalogen compounds, probably the least is known about oxyiodine chemistry. The literature contains few studies of reactions whose mechanisms contain elementary processes involving oxyiodine species. The more notable reaction systems of this type are: The Dushman Reaction, iodate-iodine isotopic exchange, iodine hydrolysis, and the reduction of iodate by hydrogen peroxide. In addition, the Bray-Liebhafsky reaction, which is a homogeneous chemical oscillator, involves oxyiodine chemistry. Some or all of these systems may exhibit common kinetic features with reaction (1). A consideration of their kinetics may benefit the present study. This section summarizes past work concerning these oxyiodine reaction systems. The survey illustrates
the complex nature of oxyiodine chemistry and the consequent need for research into its understanding.

1. Iodine Hydrolysis

Hydrolysis of elementary iodine proceeds by equation (2).

\[
I_2(aq) + H_2O \xrightleftharpoons{k_f \over k_r} I^-(aq) + HOI(aq) + H^+(aq)
\]

\(k_f\) and \(k_r\) are rate constants for the forward and reverse reactions. Allen and Keefer\(^2\) determined the hydrolysis equilibrium constant to be \(4.3 \times 10^{-13}\) M\(^{-2}\) at 20°C. Iodine hydrolysis is probably the best understood reaction considered in this survey. Its kinetics were recently explored by Eigen and Kustin\(^3\) using a temperature jump relaxation technique. They found the rate constant \(k_f\) to be 2.1 sec\(^{-1}\) while \(k_r\) was determined to be \(3.0 \times 10^{12}\) M\(^{-2}\) sec\(^{-1}\). Both rate constants were measured at 20°C and an ionic strength of 0.1 M. Eigen and Kustin propose the scheme in equation (3) to explain the hydrolysis.

\[
I_2(aq) + H_2O \xrightleftharpoons{k_f \over k_r} I_2OH^-(aq) + H^+(aq)
\]

\[
\begin{align*}
&\text{HOI(aq) + H}^+(aq) + I^-\text{(aq)} \\
&\text{Since hydrolysis is capable of scavenging iodide and hypoiiodous acid in aqueous media to produce iodine, it should be considered in any mechanistic description of systems involving oxyiodine chemistry.}
\end{align*}
\]
2. Reduction of Iodate by Hydrogen Peroxide

Liebhafsky has studied the reduction of iodate by hydrogen peroxide (equation (4)) while preventing complicating side reactions by removing product iodine from the reaction medium as soon as it is formed.

\[
2\text{IO}_3^- (\text{aq}) + 2\text{H}^+ (\text{aq}) + 5\text{H}_2\text{O}_2 (\text{aq}) \rightleftharpoons 2\text{I}_2 (\text{aq}) + 6\text{H}_2\text{O} + 5\text{O}_2 (g)
\]

Extraction of iodine from the aqueous reaction medium into carbon tetrachloride suppresses its reaction with hydrogen peroxide (equation (5)) and so simplifies the kinetics of reaction (4).

\[
\text{I}_2 (\text{aq}) + 5\text{H}_2\text{O}_2 (\text{aq}) \rightleftharpoons 2\text{IO}_3^- (\text{aq}) + 2\text{H}^+ (\text{aq}) + 4\text{H}_2\text{O}
\]

Liebhafsky found a rate law of the following form for process (4):

\[
\frac{\delta(\text{I}_2)}{\delta t} = [4.3 \times 10^{-6} + 2.15 \times 10^{-4} (\text{H}^+)] (\text{IO}_3^-) (\text{HOOH})
\]

where the rate constants are reported for 50°C. The author also reports an induction period of a few minutes before attainment of the full rate.

Reaction (4) is believed to be initiated by either of two rate limiting steps. Step (7) leads to the second order term of the observed rate law, and step (8) leads to the third order term.

\[
\text{IO}_3^- (\text{aq}) + \text{HOOH(aq)} \rightleftharpoons \text{IO}_2^- (\text{aq}) + \text{H}_2\text{O} + \text{O}_2 (\text{aq})
\]
\[ (8) \text{IO}_3^-(aq) + \text{HOOH}(aq) + H^+(aq) \rightarrow \text{HIO}_2(aq) + H_2O + O_2(g) \]

The mechanism is completed by the series of steps (9) through (12), leading to the net chemical change of process (4).

(9) \[ H^+(aq) + I\text{O}_2^-(aq) \rightleftharpoons \text{HIO}_2(aq) \]

(10) \[ \text{HIO}_2(aq) + H^+(aq) + I^-(aq) \rightleftharpoons 2\text{HOI}(aq) \]

(11) \[ \text{HOI}(aq) + \text{HOOH}(aq) \rightleftharpoons I^-(aq) + H^+(aq) + H_2O + O_2(g) \]

(12) \[ \text{HOI}(aq) + I^-(aq) + H^+(aq) \rightleftharpoons H_2O + I_2(aq) \]

Step (12), the iodine hydrolysis equilibrium, is the process postulated to lead to iodine production. The induction period associated with reaction cannot be explained by Liebhafsky's Mechanism in that only the principal reactants \( \text{HOOH}, \text{IO}_3^-, \) and \( H^+ \) are involved in the rate limiting steps. It is likely that the rate limiting process should involve an intermediate species, with reaction becoming noticeable only after this intermediate's concentration has built up to a critical value.

Liebhafsky's Mechanism for reaction (4) has no path in it for producing iodide-ion. It may be this intermediate's concentration whose value must reach a critical value before reaction becomes noticeable. It is impossible to extract all of the iodine produced from the reaction mixture. We suggest that it is iodine accumulation in
the aqueous reaction medium which causes the observed induction period. As reaction (4) progresses, more and more iodine accumulates in the reaction mixture, which in turn leads to higher and higher concentrations of iodide-ion through the reverse of reaction (12). Once the iodide-ion concentration builds up to a critical value, the rate of reaction (4) becomes noticeable.

3. Dushman Reaction

The Dushman Reaction\(^5\) has been the subject of extensive study over the last 75 years. Controversy still surrounds its kinetics with no general agreement as to its rate law or mechanism. The stoichiometry of this reaction is reproduced in equation (13).

\[
(13) \quad \text{I}_3^-(aq) + 5\text{I}^- (aq) + 6\text{H}^+(aq) \rightarrow 3\text{I}_2(aq) + 3\text{H}_2\text{O}
\]

Rate laws of the fourth, fifth, and sixth orders have been proposed to describe the kinetics of process (13). This section is a summary of the literature concerning the kinetics of the Dushman Reaction.

In 1928 Abel and Hilferding\(^6\) found that at iodide concentrations greater than \(10^{-4}\) M the rate expression for the Dushman Reaction is of the form:

\[
(14) \quad \frac{\delta (\text{I}_3^-)}{\delta t} = k(\text{I}_3^-)(\text{I}^-)^2(\text{H}^+)^2
\]

while at iodide concentrations less than \(10^{-8}\) M it becomes:
Abel, et al., report \( k \) and \( k' \) to be \( 4.05 \times 10^2 \) M\(^{-4}\) sec\(^{-1}\) and \( 1.3 \times 10^9 \) M\(^{-3}\) sec\(^{-1}\) respectively at 25°C. Under the former conditions the investigators suggest equation (16) as a rate determining step of reaction.

\[
(16) \quad \text{I}O_3^-(aq) + 2\text{I}^-(aq) + 2\text{H}^+(aq) \rightarrow 2\text{HOI}(aq) + \text{IO}^-(aq)
\]

At lower iodide concentrations the rate limiting step is believed to be:

\[
(17) \quad \text{I}O_3^-(aq) + \text{I}^-(aq) + 2\text{H}^+(aq) \rightarrow \text{HOI}(aq) + \text{HOIO}(aq)
\]

These rate limiting steps are followed by a succession of fast processes leading to iodine and water.

Morgan, Peard, and Cullis\(^7\) reexamined the mechanism of the Dushman Reaction assuming the rate law found by Abel and Hilferding to be correct. Their reinterpretation attempts to explain the rate law in terms of a series of elementary steps each of which involves a structural change of a simple nature, and therefore a low entropy of activation. Their mechanism consists of an initial equilibrium between \( \text{I}O_3^- \) and \( \text{I}O_2^+ \) (equation (18)). This initial equilibrium is followed by two possible rate limiting steps, either equation (19) or (20). Step (19) corresponds to the path dominant at low iodide concentration and gives rise to rate law (15), while step (20)
corresponds to the path dominant at high iodide concentration and gives rise to rate law (14).

(18) \[ \text{IO}_3^-(aq) + 2H^+(aq) \rightleftharpoons \text{IO}_2^+(aq) + H_2O \]

(19) \[ \text{IO}_2^+(aq) + I^-(aq) \rightarrow \text{IO}^+(aq) + \text{IO}^-(aq) \text{ (low (}I^-\text{))} \]

(20) \[ \text{IO}_2^+(aq) + 2I^-(aq) \rightarrow I^+(aq) + 2\text{IO}^-(aq) \text{ (high (}I^-\text{))} \]

It is curious that step (20) is termolecular and must therefore have a high entropy of activation. Nevertheless, this mechanism reproduces the experimentally observed rate law of Abel and Hilferding.

Myers and Kennedy\(^8\) have investigated the kinetics of the exchange of iodine atoms between molecular iodine and iodate in acid solution (equation (21)).

(21) \[ I^-\text{I}^{131}(aq) + \text{IO}_3^-(aq) \rightleftharpoons I^-I(aq) + I^{131}\text{O}_3^-(aq) \]

The rate of exchange was monitored by following the rate of disappearance of radioactive iodine \(^{131}\text{I}\) atoms from initially labelled molecular iodine. The authors first determined a rate expression involving non-integral orders in \(I^-\), \(\text{IO}_3^-\), \(H^+\), and \(I_2\). They then used the Dushman Equilibrium expression to eliminate the iodine term in the rate expression. The following rate law for exchange at 25°C results:

(22) \[ \frac{1}{3} \frac{\delta(I_2)}{\delta t} = [4.42 \times 10^8 (\text{IO}_3^-) + 6.60 \times 10^6 (\text{ClO}_4^-)] (H^+)^3 (I^-)(\text{IO}_3^-) \]
Therefore, from the equilibrium exchange reaction, Myers and Kennedy claim they have derived a rate law for the Dushman Reaction (equation (22)).

However, just because the Dushman Reaction equilibrium constant expression was used in the derivation of rate law (22) does not require the exchange to proceed through the mechanism of the Dushman Reaction. In fact, any equilibrium expression involving species in the reaction mixture may be used in the derivation of a rate law for the exchange since the exchange is always at equilibrium. Rate law (22) raises the possibility that perchlorate-ion may be important to the kinetics of oxyiodine reaction systems.

Myers and Kennedy propose the following mechanism to explain their rate law:

\[(23) \quad H^+(aq) + IO_3^-(aq) \rightleftharpoons HIO_3(aq)\]
\[(24) \quad HIO_3(aq) + H^+(aq) \rightleftharpoons IO_2^+(aq) + H_2O\]
\[(25) \quad IO_2^+(aq) + X^-(aq) \rightleftharpoons IO_2^+X^-(aq)\]
\[(26) \quad H^+(aq) + I^-(aq) \rightleftharpoons H^+I^-(aq)\]
\[(27) \quad IO_2^+X^-(aq) + H^+I^-(aq) \rightarrow HOIO(aq) + I^+X^-(aq)\]

The products HOIO and I^+X^- then go on to react rapidly with hydroiodic acid to give water, iodine, and X^- . X^- represents either an iodate or perchlorate-ion. Step (27) is rate limiting and is preceded by four equilibria.
generating the reactant species for step (27). Their mechanism consists of two parallel reaction schemes leading to products, one corresponding to $X^- = \text{ClO}_4^-$ and the other to $X^- = \text{IO}_3^-$. Therefore, the mechanism leads to the two term rate law found experimentally (equation (22)).

More recent investigations of process (13) at iodide concentrations below $10^{-8}$ M indicate the rate law is of the fourth or fifth order. Furuichi and Liebhafsky maintained the iodide concentration at low values (<$10^{-8}$ M) by establishment of an equilibrium between silver iodide and silver iodate in the reaction medium. They found the rate law in equation (28) described their experiments.

\[(28) \quad \frac{1}{3} \frac{\delta (I_2)}{\delta t} = k (H^+)^2 (I^-) (\text{IO}_3^-)\]

In equation (28) $k$ is reported to be $1.43 \times 10^3$ M$^{-3}$ sec$^{-1}$ at 25°C. Equation (28) agrees in form with that found by Abel and Hilferding at low iodide concentrations. Equation (28) is not unique in describing the experimental data of Furuichi and Liebhafsky. These authors found the following rate law describes the experimental data equally as well as equation (28):

\[(29) \quad \frac{1}{3} \frac{\delta (I_2)}{\delta t} = [6.6 \times 10^6 + 2.8 \times 10^5 (\text{IO}_3^-)] (H^+)^2 (I^-)(\text{IO}_3^-)\]

where the rate constants are reported for 25°C. Furuichi and Liebhafsky believe the dimeric species $\text{H}_2\text{I}_2\text{O}_6$ exists
in the reaction medium, and that iodide probably reacts with it. Consideration of this additional fate of iodide leads to the second term in equation (29) as opposed to the single term rate law of equation (28).

These investigators postulate the following reaction scheme to explain equation (29):

\[
\begin{align*}
(30) \quad & H^+(aq) + I^-(aq) + HIO_3(aq) \leftrightarrow H_2I_2O_3(aq) \\
(31) \quad & H_2I_2O_3(aq) \rightarrow HOI(aq) + HOIO(aq)
\end{align*}
\]

where the decomposition of \( H_2I_2O_3 \) is rate limiting. In addition the following path may lead to reaction:

\[
\begin{align*}
(32) \quad & 2HIO_3(aq) \leftrightarrow H_2I_2O_6(aq) \\
(33) \quad & H^+(aq) + I^-(aq) + H_2I_2O_6(aq) \rightarrow 3HOIO(aq)
\end{align*}
\]

where the reaction between iodide and the dimer \( H_2I_2O_6 \) is rate limiting. Both reaction paths include the iodate, iodic acid equilibrium.

In the same paper Furuichi and Liebhafsky\(^9\) reexamine the data of Abel and Hilferding and Myers and Kennedy and show those authors' data to be consistent with equations (28) and (29). The investigators also experimentally refute the first order perchlorate-ion dependence found by Myers and Kennedy. They show the rate of the Dushman Reaction to be independent of the perchlorate-ion concentration. This last fact casts doubt on the hypothesis that the iodine, iodate exchange has the same rate limiting step as the Dushman Reaction.
Schildcrout and Fortunato\textsuperscript{10} studied reaction (13) at 25°C in acetic acid, potassium acetate buffered solution. A buffer was employed in order to maintain the acidity of the reaction medium at a constant, low value ($\sim 10^{-1}$ M) throughout the course of reaction. They varied the iodide concentration between $10^{-2}$ M and $10^{-4}$ M. Their rate law is given in equation (34).

\begin{equation}
\frac{1}{3} \frac{\delta (I_2)}{\delta t} = (2.6 \times 10^6 + 4.2 \times 10^8 (I^-)) (I_3^-) (I^-)^2 (H^+)^2
\end{equation}

The fourth order term of equation (34) is identical to the fourth order term in the rate laws found by Abel and Hilferding and Furuichi and Liebhafsky. In equation (34) the fourth order term dominates at low iodide concentrations as found by Abel, et. al., and Furuichi, et. al. Schildcrout and Fortunato interpret their rate law in terms of the mechanism proposed by Morgan, Peard, and Cullis.

Sharma and Gupta\textsuperscript{11} also investigated the kinetics of the Dushman Reaction and report the rate law of equation (35).

\begin{equation}
\frac{1}{3} \frac{\delta (I_2)}{\delta t} = k(I_3^-) (I^-) (H^+)^2 / (1 + k' (H^+)^2)
\end{equation}

In equation (35) $k$ and $k'$ have the values $4.8 \times 10^5$ M$^{-2}$ sec$^{-1}$ and $1.5$ M$^{-1}$ sec$^{-1}$ at 35°C. Their experiments were performed in the presence of phenol, and the possibility exists that phenol may participate in the kinetics.
Previous investigations of the Dushman Reaction come to no general agreement as to the mechanism by which it proceeds, with a variety of intermediates proposed to lead to reaction. However, a comparison of the rate laws proposed for the reaction reveals a degree of consistency between them. Figure (1) is a plot of \(-\log (\text{RATE})\) versus pI for the rate laws reported by Abel, Schildcrout, and Liebhafsky (equations (14) and (15), (28), and (34) respectively). The plot is constructed for an acid concentration and iodate concentration near the experimental ranges within which the rate laws were determined. Each rate law is plotted only over the range of pI within which it was determined. As figure (1) shows the three rate laws agree well with each other. The fifth order term reported by Abel and Schildcrout dominates at iodide concentrations above \(10^{-4}\) M, while the fourth order term reported by Abel and Liebhafsky dominates at iodide concentrations below \(10^{-8}\) M. Despite some confusion in the literature concerning the Dushman Reaction, this reaction must be important in the mechanistic description of any oxyiodine reaction system.

4. Bray Liebhafsky Reaction

Information concerning the kinetics of oxyiodine systems is particularly important now that mechanisms for the Bray-Liebhafsky Reaction\(^{12}\) are being discussed.
Figure (1): A plot of $-\log(\text{rate})$ versus $\text{pI}$ for the various rate laws reported for the Dushman Reaction. The three curves are plots of equations (14) and (15), (28), and (34). Temperature = 25°C.
The Bray-Liebhafsky Reaction is the iodate catalyzed decomposition of hydrogen peroxide (equation (36)).

\[ \text{(36)} \quad 2\text{HOOH(aq)} \xrightarrow{\text{IO}_3^-} \text{O}_2(g) + 2\text{H}_2\text{O} \]

Reaction (36) is unusual since it is one of only a handful of known homogeneous chemical oscillators. Figure (2) illustrates oscillations which occur in the concentration of molecular iodine and iodide. Oxygen gas is also evolved from the reaction medium in pulses. These oscillations do not occur about the final equilibrium state of the system, but circle an unstable steady state far from equilibrium. A mechanism for the Bray Liebhafsky Reaction which qualitatively explains the oscillations has been proposed by Sharma and Noyes. Their mechanism consists of the two complex processes shown in equations (37) and (38).

\[ \text{(37)} \quad 2\text{IO}_3^-(aq) + 5\text{HOOH(aq)} + 2\text{H}^+ \xrightarrow{} \text{I}_2(aq) + 5\text{O}_2(g) + 6\text{H}_2\text{O} \]

\[ \text{(38)} \quad \text{I}_2(aq) + 11\text{HOOH(aq)} \xrightarrow{} 2\text{IO}_3^-(aq) + 3\text{O}_2(g) + 2\text{H}^+(aq) + 10\text{H}_2\text{O} \]

Process (37) is dominated by non-radical elementary steps, while process (38) is dominated by radical reactions. Process (38) operates in part through a radical chain mechanism and is autocatalytic in the production of the intermediate species HOIO. Reactions (37) and (38) both proceed via complex mechanisms, each involving elementary
Figure (2): Plots of pH and (I₂) versus time (minutes) for the Bray Liebhafsky Reaction. Temperature = 50°C. Plots reproduced from reference 13.
steps between oxyiodine species. The two processes are coupled through common intermediates producing a scheme by which they alternate in dominance, thereby giving rise to the observed oscillations. Although the Sharma-Noyes Mechanism of the Bray-Liebhafský Reaction can qualitatively account for the oscillations, quantitative confirmation of the mechanism has been hindered by the limited information available on oxyiodine chemistry. The ultimate test of their mechanism is the successful numerical reproduction of the observed oscillations based on rate data reported in the literature. Such data is now scarce, and this is mainly the reason for which this work was undertaken.

C. PREVIOUS WORK ON THE OXIDATION OF FERROUS ION BY IODATE

Mitzner, Fischer, and Leupold\textsuperscript{1} interpreted their data by assuming that the following rate law describes the kinetics of oxidation at 25°C:

\begin{equation}
\frac{1}{10} \frac{\delta (\text{Fe(II)})}{\delta t} = k_{\text{exp}} (\text{IO}_3^-)
\end{equation}

where,

\[
k_{\text{exp}} = k_1 + k_2 (H^+) + k_3 (H^+) (I_2)_0 + 2k_2 (H^+) (\text{IO}_3^-) - 2k_2 (\text{IO}_3^-) (H^+)
\]

They also found the reaction to be autocatalytic, with accumulated iodine increasing the rate of reaction. To explain these results Mitzner, et. al., propose a rate limiting step in which iodic acid formed in an equilibrium
with iodate and hydrogen-ion decomposes into $\text{IO}_2^+$ and $\text{OH}^-$. This initiation scheme is illustrated in equations (40) and (41).

\[
(40) \quad \text{H}^+(\text{aq}) + \text{IO}_3^-(\text{aq}) \rightleftharpoons \text{HIO}_3(\text{aq})
\]

\[
(41) \quad \text{HIO}_3(\text{aq}) \rightarrow \text{IO}_2^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad \text{(rate limiting)}
\]

These two initial steps are followed by a series of rapid one-electron transfers between Fe(II) and the oxyiodine intermediates $\text{IO}_2^+$, $\text{IO}_2$, $\text{HIO}_2$, $\text{IO}$, and $\text{HOI}$ to produce the reaction products. Process (42) was proposed by them to initiate the path responsible for autocatalysis.

\[
(42) \quad \text{HIO}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{HOI}(\text{aq}) + 2\text{IO}(\text{aq})
\]

Both oxyiodine products generated by this process are reduced to iodine by Fe(II) producing the experimentally observed autocatalysis. Even though reaction (42) does explain the autocatalytic production of iodine, the steric requirement in the transition state for the initiation reaction may be prohibitive in that it is a five-centered encounter (equation (43)).

\[
(43) \quad \text{HIO}_3 + \text{I}_2 \rightarrow \text{HOI(I)} \quad \text{HOI} \quad 0 \quad \text{I} \quad \text{HOI} + 2\text{IO}
\]

An alternative path leading to autocatalysis is likely.

The manner in which these investigators interpreted their data is obviously incorrect and leads to incorrect conclusions concerning the form of the rate law. Thus, little credence can be placed in their mechanistic
conclusions. They determine an order in Fe(II) based on plots of -log (Fe(II)) versus time which cover only 60% of reaction. Plots of integrated rate expression covering less than 90% completion of reaction are essentially useless since mostly any rate expression will give a reasonable straight line up to 60%-70% reaction. It is the constancy of rate constants for runs covering a wide range of initial reactant concentrations that demonstrates the validity of a rate expression. Mitzner, et. al., did not make kinetic runs covering a wide range of initial reactant concentration. Thus, their rate expressions may very well be in error. Our finding of an order in Fe(II) close to 1.0 shows their rate law to be incorrect (equation (39)), and therefore invalidates any mechanistic conclusion based on it.
CHAPTER II

METHODS AND MATERIALS

A. CHEMICALS AND ANALYTICAL PROCEDURES

All chemicals employed in the study were used as received from the chemical manufacturer with no further purification. Solid chemicals were weighed out on a Mettler H-51 single pan balance.

Sodium iodate was Mallinckrodt Analytical Reagent grade. Prior to an experiment, it was dried for at least one hour at 110°C, and then weighed out to the nearest one-hundredth of a milligram.

Hydrated ferrous perchlorate \((\text{Fe(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O})\) was Matheson, Coleman, and Bell reagent grade. Stock solutions of ferrous perchlorate were made up to an approximate molarity and then analyzed. Prior to an initial rate study the initial ferrous-ion concentration was determined by a potassium dichromate titration to a diphenylamine endpoint. The titration analysis was always done in triplicate. For experiments in which the entire course of reaction was monitored, the initial ferrous-ion concentration was analyzed spectrophotometrically through complexation with 1,10 orthophenanthroline. The Fe(II) complex of ortho phenanthroline was found to have an
absorption maximum at 508 nm and an extinction coefficient of 11,200 M\(^{-1}\). Spectrophotometric analysis was performed in duplicate for each ferrous-ion stock solution prepared. Complexation of Fe(II) is quantitative in the pH range 2-9.\(^{15}\) When necessary, pH adjustment was accomplished using one molar sodium hydroxide. A complete description of the 1,10 orthophenathroline analysis for Fe(II) is given elsewhere.\(^{15}\)

72% (by weight) perchloric acid was Baker Analyzed reagent grade. It was analyzed by titration with a solution of sodium hydroxide which had been standardized against potassium hydrogen phthalate. Analysis was done in triplicate for each perchloric acid stock solution. Phenolphthalein served as an indicator in these titrations.

Aqueous iodine stock solutions were prepared from crystalline iodine manufactured by the J.T. Baker Corporation. The iodine concentration was then analyzed spectrophotometrically at \(\lambda_{\text{MAX}} = 466\) nm, \(\varepsilon(\text{Iodine}) = 700\) M\(^{-1}\) cm\(^{-1}\).

Once the principal reactants had been measured out and their concentrations analytically determined, the ionic strength of the reaction media was adjusted to 1.5 M with sodium perchlorate monohydrate. All kinetic runs of this investigation were carried out at an ionic strength of 1.5 M. Sodium perchlorate came from the
Matheson, Coleman, and Bell Laboratories. It was weighed out directly without drying.

All stock solutions which were eventually to be used as components of the reaction medium were prepared using triply distilled water. Such purification was carried out to insure that no stray catalysts contaminated the reaction mixture. The distillation apparatus was constructed completely from glass. It consisted of a sodium dichromate stage, a potassium permanganate stage, and a trap, followed by a final distillation from the trap into a storage container. Additionally, all stock solutions were purged with dry nitrogen before they were introduced into the reaction mixture.

B. METHODS

1. Initial Rate Experiments

The initial rate experiments were carried out in a ground glass stoppered erlenmeyer flask containing a 25 ml glass tube insert joined to the bottom of the flask. The reaction flask therefore contained two separate compartments. Two 100 ml stock solutions were prepared, one containing ferrous perchlorate in one molar perchloric acid and the other sodium iodate and sodium perchlorate in one molar perchloric acid. 20 ml of each stock solution was then introduced into the separate compartments of the reaction flask. The flask was stoppered
and equilibrated to 30.0 ± 0.2°C in a constant temperature water bath for at least two hours. After equilibration the flask was shaken in order to mix its contents. Within one minute of mixing a small quantity of the reaction mixture was transferred to a 1 cm path length silica spectrophotometer cell which had previously been equilibrated to 30.0 ± 0.2°C in the Beckman Model D.U. Spectrophotometer cell compartment. The absorbance of product iodine was followed as a function of time. All reaction runs were followed to at least 50% completion, however calculation of the initial rate of reaction was based on data collected within only the first 10% of reaction. For runs at acid concentrations different from one molar each 100 ml stock solution contained the appropriate amount of perchloric acid.

The Beckman Spectrophotometer was outfitted with thermospacers, into which water flowed from a Haake Model FE thermostated water circulator. All initial rates studied were run at 30.0 ± 0.4°C.

2. Iodine Extraction Experiments

The procedure for following the reaction over its entire course while continuously removing iodine from the reaction medium consisted of first preparing two 250 ml stock solutions, one containing perchloric acid and ferrous perchlorate, the other sodium iodate and
sodium perchlorate. 75 ml of each stock solution was transferred into two separate glass, round bottom flasks. These flasks were first stoppered and then clamped into a constant temperature water bath. At the same time a 300 ml erlenmeyer flask fitted with a rubber stopper was clamped in the same constant temperature water bath. This flask contained 150 ± 25 ml of analytical grade carbon tetrachloride and a magnetic stirring bar. All flasks were equilibrated to 30.0 ± 0.2°C for at least two hours, after which time the contents of the two flasks containing the principal reactants were mixed. Timing of reaction progress started at the instant of mixing. The reaction mixture was quickly transferred to the 300 ml erlenmeyer flask contained in the water bath. The contents of the flask were stirred by use of a Corning Model PC-351 Magnetic Stirrer situated directly under the reaction flask and supporting the water bath. In this manner iodine was continuously extracted from the aqueous reaction layer into the inert carbon tetrachloride layer as rapidly as it was formed. At 25°C the partition coefficient of iodine between carbon tetrachloride and water is 85, and therefore the iodine concentration is always essentially zero in the reaction medium (0.0 M < (I₂) < 4.7 x 10⁻⁵ M for runs involving the greatest iodine production). Depending on the initial concentration of reactants, stirring was interrupted periodically
and 5 ml of reaction mixture pipetted into a volumetric flask containing water and 1,10 orthophenanthroline complexing agent. The minimum dilution of a reaction aliquot was 20-fold, however the complexation of Fe(II) with orthophenanthroline also served to quench reaction. The resulting orange solutions were analyzed on a Coleman-Hitachi Model E.P.S. 3-T, U.V.-Visible Spectrophotometer, and concentration of Fe(II) as a function of time data derived.

3. Iodine Accumulation Experiments

For runs in which iodine was allowed to accumulate in the reaction medium, we followed an identical procedure to that used in the iodine extraction experiments, except that the carbon tetrachloride and magnetic stirring bar were not added to the reaction flask. Absorbance due to iodine was neglected in the spectrophotometric analysis of the resulting 1,10 orthophenanthroline complex solutions. In no experiment did solid iodine precipitate from the reaction medium. All accumulation experiments were done at 30.0 ± 0.2°C and an ionic strength of 1.5 M.

For each iodine accumulation experiment as well as for each iodine extraction experiment the concentration of Fe(II) was monitored through at least 80% of reaction.
4. Numerical Simulation of Experiments

Numerical simulation of our postulated mechanism was carried out on the Dec System 20 Computer owned by the University of Montana. Simulation consisted of writing out the rate expressions for the various chemical species in the mechanism. This procedure leads to a system of simultaneous, first order, ordinary differential equations (11 for our mechanism). Values for rate constants were assigned to individual elementary processes and the system of differential equations was integrated using the Ordinary Differential Equation Solver developed by Gear. Results of integrations were plotted out on a Hewlett-Packard 7200-A Graphic Plotter as (Fe(II)) versus time, -log ((Fe(II))) versus time, or (I₂) versus time. The numerically generated plots were compared with those generated experimentally. Concentrations of all intermediates were output by the computer program at regular time intervals.
CHAPTER III

RESULTS AND DISCUSSION

A. RESULTS

1. Initial Rates

The advantage of an initial rates study is the elimination of effects from complicating side reactions which may become important as products accumulate. In the present study information can be gathered about the kinetics of process (1) without contending with the complicating influence of autocatalysis. A limitation of the initial rates procedure is that the information so obtained only pertains to the kinetics of initial processes and cannot be safely extrapolated to the kinetics at later stages of reaction. Nevertheless, initial rates serves as a logical method with which to study a complicated reaction system such as reaction (1).

An experimental problem which arises while using an initial rates technique is initial equilibration of the reaction mixture with respect to homogeneity of solution composition and temperature fluctuation. Both of these problems are most prevalent in the initial stages of any experimental run as opposed to later in that run when equilibration is complete. In all our experiments the
two reactant solutions were thoroughly mixed for nearly one minute. Thus, composition homogeneity was likely achieved very early in any given run. On the other hand, our experimental technique involved two constant temperature water baths held at $30.0 \pm 0.2 \, ^\circ C$. One of these was used to equilibrate the reactants to $30.0 \pm 0.2 \, ^\circ C$ before their mixing, while the other was hooked up to the spectrophotometer cell compartment in order to keep the reaction mixture at $30.0 \pm 0.2 \, ^\circ C$ during the course of a run. While mixing the reactants together the reaction solutions were not in a $30.0 \pm 0.2 \, ^\circ C$ water bath, but were held in an environment at $25\, ^\circ C$ (room temperature). Thus, during mixing the temperature of the reaction solution probably dropped below $30.0 \pm 0.2 \, ^\circ C$. Additionally, small differences in temperature probably existed between the two water baths employed in the experiments. For these reasons we report our initial rate results for a temperature of $30.0 \pm 0.4 \, ^\circ C$, with the relatively large experimental error reflecting uncertainties in the initial temperature of the reaction solution.

The initial slope of an absorbance versus time plot for any given run yields the initial rate of that run. Initial reaction is defined by us to encompass the first $10\%$ of reaction, and we therefore considered only those data points within the first $10\%$ of reaction in calculating
our initial rates. A typical plot of absorbance versus time data is illustrated in figure (3), along with the initial rates line.

Table (I) shows the results of experiments developed to test the effect of oxygen on the initial rate of reaction. Purging the reaction mixture with either nitrogen or oxygen does not give different initial rates for otherwise identical runs. Thus the initial reaction rate is independent of the oxygen content of the reaction medium.

Initial orders in the principal reactants are found by use of the following rate expression:

\[
\frac{1}{10} \frac{\delta (\text{Fe(II)})}{\delta t} = k_{\text{exp}} (\text{Fe(II)})^a_0 (\text{I}_3^-)^b_0 (\text{H}^+)^c_0 (\text{I}_2)^d_0
\]

where \((\text{Fe(II)})^a_0\) stands for the initial concentration of ferrous-ion raised to an undetermined order \(a\). Analogous definitions of the three remaining terms apply; \(b\), \(c\), and \(d\) being the initial orders in iodate, hydrogen-ion, and iodine respectively. \(k_{\text{exp}}\) is the initial rates experimental rate constant. The unknown order \(a\) is evaluated by making a series of runs, each involving a different ferrous-ion concentration. Initial concentrations of other principal reactants are kept constant throughout the series of runs. In this manner we gather initial rate as a function of ferrous-ion concentration data.
Iodine

ABS.

(Fe(II))₀ = 0.0312 M
(IO₃⁻)₀ = 0.00413 M
(H⁺)₀ = 1.0 M

Initial Rate = 0.0085 ABS units/min

Figure (3): A plot of iodine absorbance versus time in minutes. The slope of the line drawn through the points within the first 10% of reaction corresponds to the initial rate. Temperature = 30.0 ± 0.4 °C, ionic strength = 1.5.
The effect of oxygen on the initial reaction rate. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5.

Initial concentrations for trials 1 and 2:

\[(\text{IO}_3^-)_o = 0.0043 \text{ M}, \ (\text{Fe(II)})_o = 0.015 \text{ M}, \ (\text{H}^+)_o = 1.0 \text{ M}\]

Initial concentrations for trials 3 and 4:

\[(\text{IO}_3^-)_o = 0.0043 \text{ M}, \ (\text{Fe(II)})_o = 0.046 \text{ M}, \ (\text{H}^+)_o = 1.0 \text{ M}\]

<table>
<thead>
<tr>
<th>Trial NO.</th>
<th>Gas Present in Reaction Medium</th>
<th>Initial Rate (ABS/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N(_2)</td>
<td>.0019</td>
</tr>
<tr>
<td>2</td>
<td>O(_2)</td>
<td>.0018</td>
</tr>
<tr>
<td>3</td>
<td>N(_2)</td>
<td>.0155</td>
</tr>
<tr>
<td>4</td>
<td>O(_2)</td>
<td>.0152</td>
</tr>
</tbody>
</table>
If \( k_{\text{exp}} \) and the concentrations which remain constant from run to run are gathered into the constant \( kz_{\text{ap}} \), we arrive at expression (45).

\[
\frac{1}{10} \frac{\delta(\text{Fe(II)})}{\delta t} = kz_{\text{ap}} (\text{Fe(II)})_o^a
\]

\[
kz_{\text{ap}} = k_{\text{exp}} (\text{IO}_3^-)_o^b (\text{H}^+)_o^c (\text{I}_2)_o^d
\]

Equation (45) may be rearranged into the form of expression (46).

\[
\log_{10}(\text{RATE}) = \log_{10}(kz_{\text{ap}}) + a \log_{10}((\text{Fe(II)})_o)
\]

A plot of \( \log_{10}(\text{RATE}) \) versus \( \log_{10}((\text{Fe(II)})_o) \) leads to a straight line of slope \( a \). Strictly analogous procedures give the remaining orders \( b, c, \) and \( d \). Typical log-log order plots are illustrated in figures (4), (5), and (6). The slopes of the log-log plots are calculated by a least squares data fit.

The results of initial rate studies for runs in which no iodine is initially present in the reaction medium are summarized in Table (II). At a temperature of 30.0 ± 0.4°C the initial rate may be expressed as:

\[
\frac{1}{10} \frac{\delta(\text{Fe(II)})}{\delta t} = k_{\text{exp}} (\text{Fe(II)})_o^{1.15\pm.02} (\text{IO}_3^-)_o^{0.98\pm.02} (\text{H}^+)_o^{1.00\pm.03}
\]

In figure (6), if the data point at an acid concentration of 0.1 M is neglected the least squares line through the remaining data points gives an order with respect to hydrogen-ion of 1.00 ± .03. The order of 1.15 ± .02 in
1.0
1.2
1.4
Q J
M
n J
1.6
r — j
( Ü
•H
■ P
•H
1.0
2.0
2.2
2.4
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
- log (Fe(II))_o
- log(initial rate)

(%O_3^-)_o = 0.0413 M
(H^+)_o = 1.0 M
slope = a = 1.15 \pm 0.02

Figure (4) : A plot of -log(initial rate) versus -log((Fe(II))_o).

The slope of the line as determined by a least squares method is the
initial order in Fe(II). Temperature = 30.0 \pm 0.4 \degree C, ionic strength = 1.5.
Figure (5): A plot of log(initial rate) versus log \((\text{IO}_3^-)_o\).

Temperature = 30.0 ± 0.4 °C, ionic strength = 1.5.
Figure (6) : A plot of log(initial rate) versus log\((\text{H}^+)_0\). The slope as determined by a least squares method gives the order, \(c\), in acid. The data point at the lowest acid concentration has been neglected in the order determination. Temperature = 30.0 ± 0.4 °C, ionic strength = 1.5.

\((\text{Fe(II)})_0 = 0.0385 \text{ M}\)

\((\text{IO}_3^-)_0 = 0.00414 \text{ M}\)

slope = \(c = 1.00 \pm 0.03\)
ferrous-ion is found in three separate determinations, which leads us to the conclusion that this non-integral order is real. A non-zero order in ferrous-ion contradicts the conclusion of Mitzner, et al., that the order in this reactant is zero. The orders with respect to iodate and acid are sufficiently close to one that they probably have this integral value.

The summary of Table (II) also shows that the initial order in iodine is 0.15 ± .02. This determination was of course done in the presence of initially added iodine. A plot of iodine absorbance versus time for a series of initial iodine concentrations is shown in figure (7). The plot clearly shows that iodine enhances the initial rate of reaction.

Another pertinent experiment is the determination of initial reaction orders of iodate, ferrous-ion, and hydrogen-ion in the presence of initially added iodine. The results of these experiments are summarized in Table (III). The orders in Fe(II) and IO₃⁻ drop significantly from their values when iodine is not present in the reaction mixture initially. Iodate, iodine, and ferrous-ion must therefore be involved in the observed autocatalysis. No determination of the effect of added iodine on the initial acid dependence was performed.
TABLE II.

A summary of the initial orders in the reactants Fe(II), IO₃⁻, and H⁺ when no iodine is present in the reaction medium initially. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5.

* The number in parenthesis next to a particular experimental order is the number of runs which were done for that determination.

** The acid order is based on a linear least squares fit to all the data points but the one at lowest acid (.102 M).

<table>
<thead>
<tr>
<th>Range of (Fe(II))₀</th>
<th>Range of (IO₃⁻)₀</th>
<th>Range of (H⁺)₀</th>
<th>Range of (I₂)₀</th>
<th>Initial orders a, b, c, or d</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0886-.0148</td>
<td>.00597</td>
<td>1.0</td>
<td>0.00</td>
<td>a=1.13 (6) *</td>
</tr>
<tr>
<td>.0872-.00413</td>
<td>.00413</td>
<td>1.0</td>
<td>0.00</td>
<td>a=1.15 (10)</td>
</tr>
<tr>
<td>.0755-.00251</td>
<td>.00413</td>
<td>1.0</td>
<td>0.00</td>
<td>a=1.16 (12)</td>
</tr>
<tr>
<td>.109</td>
<td>.0125-.00104</td>
<td>1.0</td>
<td>0.00</td>
<td>b=0.99 (7)</td>
</tr>
<tr>
<td>.0758</td>
<td>.00816-.0016</td>
<td>1.0</td>
<td>0.00</td>
<td>b=0.98 (5)</td>
</tr>
<tr>
<td>.0385</td>
<td>.00414</td>
<td>1.32-.102</td>
<td>0.00</td>
<td>c=1.00 (8) **</td>
</tr>
<tr>
<td>.0165</td>
<td>.0104</td>
<td>1.0</td>
<td>0.000</td>
<td>d=0.14 (4)</td>
</tr>
<tr>
<td>.0355</td>
<td>.00412</td>
<td>1.0</td>
<td>-.000567</td>
<td>d=0.16 (4)</td>
</tr>
</tbody>
</table>
Figure (7) : Kinetic runs at three different initial iodine concentrations. Temperature = 30.0 ± 0.4 °C, ionic strength = 1.5.

- $\Box (I_2)_0 = 0.00 \text{ M}$ initial rate = .0084 $\frac{\text{ABS}}{\text{min}}$
- $\bigcirc (I_2)_0 = 2.1 \times 10^{-4} \text{ M}$ initial rate = .0130 "
- $\bigtriangleup (I_2)_0 = 5.7 \times 10^{-4} \text{ M}$ initial rate = .0151 "

$\text{Fe(II)}_0 = 0.0355 \text{ M}$

$\text{IO}_3^-_0 = 0.00419 \text{ M}$

$\text{H}^+_0 = 1.0 \text{ M}$
TABLE III.

Initial orders in Fe(II) and IO₃⁻ in the presence of an initial iodine concentration. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5.

* The number in parenthesis next to an experimental order is the number of runs which were done for that order determination.

<table>
<thead>
<tr>
<th>Range of (Fe(II))₀</th>
<th>Range of (IO₃⁻)₀</th>
<th>Range of (H⁺)₀</th>
<th>Range of (I₂)₀</th>
<th>Initial order (a or b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0971 - 0.0162</td>
<td>0.00569</td>
<td>1.0</td>
<td>0.00037</td>
<td>a = 0.94 (6)*</td>
</tr>
<tr>
<td>0.0543</td>
<td>0.0118 - 0.00196</td>
<td>1.0</td>
<td></td>
<td>b = 0.89 (6)</td>
</tr>
</tbody>
</table>
2. Experiments Involving Iodine Extraction

The aim of the extraction experiments is to determine a rate law describing the entire course of reaction when iodine is removed from the reaction medium as soon as it is formed. Since iodine is not present at any appreciable concentration during the course of these experiments (0.0 M < (I₂) < 4.7 x 10⁻⁵ M for runs involving the greatest iodine production), complications due to autocatalysis are avoided. The extraction experiments cover a broad range of ((IO₃⁻)/(Fe(II)))₀ (0.27-208), while the hydrogen-ion concentration ranges between 0.556 M and 1.44 M.

a. Experiments at low ((IO₃⁻)/(Fe(II)))₀

At low ((IO₃⁻)/(Fe(II)))₀ (<4.0) the rate data were fit to a second order rate law of the form:

\[
\frac{1}{10} \delta \frac{\delta (Fe(II))}{\delta t} = k(Fe(II))(IO₃⁻)
\]

where the rate constant k depends on acid concentration. The integrated form of equation (48) is shown in equation (49).

\[
(49) - \log \left[\frac{(IO₃⁻)₀ - 2(Fe(II))₀}{(Fe(II))₀}\right] + 2 = \log \left(\frac{2(Fe(II))₀}{(IO₃⁻)₀}\right) + \log \left[10(IO₃⁻)₀ - 2(Fe(II))₀\right] k
\]

A representative plot of data fit to equation (49) is shown in figure (8). The slight convex curvature of this
Figure (8): A typical plot of data fit to the second order integrated rate law of equation (49). Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5 M.

\[
\begin{align*}
(\text{Fe(II)})_0 &= 0.0458 \text{ M} \\
(\text{IO}_3^-)_0 &= 0.0137 \text{ M} \\
(\text{H}^+)_0 &= 1.0 \text{ M}
\end{align*}
\]
plot away from a straight line is characteristic of low 
\( (\text{IO}_3^-)/(\text{Fe(II)})_o \) experiments, and probably arises from 
autocatalysis by residual iodine. At the high initial 
ferrous-ion concentration of these runs (>0.0127 M) an 
appreciable amount of iodine is produced. At 25°C the 
partition coefficient of iodine between water and carbon 
tetrachloride is 85. Therefore, a significant amount of 
iodine is not extracted from the aqueous reaction layer 
into carbon tetrachloride resulting in a reaction rate 
accelerated beyond that predicted by equation (48).

Table (IV) summarizes the values of k calculated for 
a series of experiments in which the acid concentration 
was maintained at a constant value near one molar. The 
absolute value for the acid concentration was not deter-
mined. These experiments covered an \( (\text{IO}_3^-)/(\text{Fe(II)})_o \) 
range from 0.17 to 3.12. An examination of Table (IV) 
shows that k does not vary systematically with either 
increasing iodate or ferrous-ion concentration. The 
average value of k for these experiments is 1.23 M\(^{-1}\) sec\(^{-1}\) 
with a mean deviation of 0.04 M\(^{-1}\) sec\(^{-1}\). Based on this 
small value for the mean deviation and the absence of 
any trends within the group of k values we conclude that 
the rate of reaction (1) at low \( (\text{IO}_3^-)/(\text{Fe(II)})_o \) 
follows the second order rate law in equation (48). Table 
(IV) also lists k values for experiments in the low
TABLE IV.

Values for the rate constants k and k' for the low \((\text{IO}_3^-)/(\text{Fe(II)})_o\) iodine extraction experiments. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5.

* Indicates runs for which the acid concentration is close to 1.0 M, but was not analyzed accurately. All runs marked with an * were run at the same acid concentration near 1.0 M.

<table>
<thead>
<tr>
<th>((\text{IO}_3^-)/(\text{Fe(II)})_o)</th>
<th>((\text{Fe(II)})_o)</th>
<th>((\text{IO}_3^-)_o)</th>
<th>((\text{H}^+)_o)</th>
<th>(k \times 10^3 \text{ M}^{-1} \text{s}^{-1})</th>
<th>(k' \times 10^3 \text{ M}^{-2} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>.17</td>
<td>.0808</td>
<td>.0137</td>
<td>1.0*</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>.20</td>
<td>.0521</td>
<td>.0104</td>
<td>1.0*</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>.31</td>
<td>.0467</td>
<td>.0147</td>
<td>1.0*</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>.30</td>
<td>.0458</td>
<td>.0137</td>
<td>1.0*</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>.63</td>
<td>.0232</td>
<td>.0147</td>
<td>1.0*</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>3.12</td>
<td>.0127</td>
<td>.0397</td>
<td>1.0*</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>.66</td>
<td>.0246</td>
<td>.0162</td>
<td>1.13</td>
<td>1.07</td>
<td>.944</td>
</tr>
<tr>
<td>.48</td>
<td>.0270</td>
<td>.0129</td>
<td>1.41</td>
<td>1.48</td>
<td>1.05</td>
</tr>
<tr>
<td>.45</td>
<td>.0396</td>
<td>.0180</td>
<td>1.13</td>
<td>1.07</td>
<td>.944</td>
</tr>
<tr>
<td>.34</td>
<td>.0689</td>
<td>.0234</td>
<td>.564</td>
<td>.528</td>
<td>.937</td>
</tr>
<tr>
<td>.27</td>
<td>.0477</td>
<td>.0130</td>
<td>.867</td>
<td>.867</td>
<td>1.02</td>
</tr>
</tbody>
</table>
\((\text{IO}_3^-)/(\text{Fe(II)})\)_o range for which the acid concentration is accurately known.

\[ \text{b. Experiments at high } (\text{IO}_3^-)/(\text{Fe(II)})_o \]

At higher \((\text{IO}_3^-)/(\text{Fe(II)})_o\) the concentration versus time data are treated according to the pseudo first order rate law of equation (50).

\[(50) \quad \frac{1}{10} \frac{\delta(\text{Fe(II)})}{\delta t} = k_p (\text{Fe(II)})\]

\(k_p\) is a pseudo first order rate constant whose value is dependent on acid concentration as well as iodate-ion concentration. The integrated form of equation (5) is shown in equation (51).

\[(51) \quad -\ln (\text{Fe(II)}) = (\text{Fe(II)})_o - 10kpt\]

Typical plots of experimental data fit to equation (51) are illustrated in figures (9) and (10). Their linearity is characteristic of all first order plots of data for runs at high \((\text{IO}_3^-)/(\text{Fe(II)})_o\). \(k_p\) is evaluated from the slope of the least squares line through the data. In equation (50) \(k_p\) has the following iodate dependence.

\[(52) \quad k_p = k (\text{IO}_3^-)^f\]

where \(f\) is an unknown order in iodate and \(k\) is a \((f + 1)\) order rate constant dependent on acid concentration.

Figure (11) is a plot of \(\log (k_p)\) versus \(\log (\text{IO}_3^-)_o\) at an acid concentration of 1.13 \(\pm\) 0.03 M. The least squares slope of this line gives a value for \(f\) equal to 1.06 \(\pm\) 0.04. Values of \(k\) for each run are calculated by dividing \(k_p\) for
Figure (9) : A typical plot of rate data fit to equation (51). The slope as determined by a linear least squares data fit is $10(k_p)$. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5.
Figure (10): A typical plot of rate data fit to equation (51). The slope as determined by a linear least squares data fit is $10(k_p)$. Temperature = $30.0 \pm 0.2^\circ C$, ionic strength = 1.5.

$(Fe(II))_o = .0006 \, M$

$(IO_3^-)_o = .0502 \, M$

$(H^+)_o = .572 \, M$

$k_p = 2.75 \times 10^{-5} \, \text{sec}^{-1}$
slope = 1.06 ± 0.03 = iodate order

Figure (11): A plot of log ($k_p$) versus log ([IO$_3^-$]$_o$) for extraction experiments in which the acid concentration is 1.13 ± 0.03 M. The slope of this plot equals the order in iodate for runs of high ([IO$_3^-$]/(Fe(II))$_o$). Temperature = 30.0 ± 0.2°C, ionic strength = 1.5.
that run by the initial iodate concentration. Table (V) lists the values of $k_p$ and $k$ found for each run in the high $((\text{IO}_3^-)/(\text{Fe(II)}))^0$ range.

c. Rate law describing all extraction runs

Over the entire range of $((\text{IO}_3^-)/(\text{Fe(II)}))^0$ the rate law for the oxidation may be written as:

\[(53) \quad - \frac{1}{10} \frac{\delta (\text{Fe(II)})}{\delta t} = k (\text{Fe(II)}) (\text{IO}_3^-)\]

where $k$ may depend on the concentration of acid. It is clear from Tables (IV) and (V) that the value of $k$ increases as the hydrogen-ion concentration increases. In order to determine the acid dependence of $k$ we plot all our data as $\ln (k)$ versus $\ln (H^+)$. The least squares slope of the $\ln-\ln$ plot is the order in acid concentration. This plot is shown in figure (12). The dependence of $k$ on acid over the concentration range .556 M to 1.44 M is $1.08 \pm .10$ as shown in equation (54).

\[(54) \quad k = k' (H^+)^{1.08\pm.10}\]

$k'$ represents a third order rate constant. Therefore, the rate law describing the kinetics of oxidation is:

\[(55) \quad - \frac{1}{10} \frac{\delta (\text{Fe(II)})}{\delta t} = k' (\text{IO}_3^-) (\text{Fe(II)}) (H^+)\]

for hydrogen-ion concentrations between 0.556 M and 1.44 M. Values of $k_p$, $k$, and $k'$ for each run are listed in Tables (IV) and (V). The average value of $k'$ based on
TABLE V.

Values of $k_p$, $k$, and $k'$ for iodine extraction experiments of high $((\text{IO}_3^-)/(\text{Fe(II)})_o$.
Temperature = 30.0 ± 0.2°C, ionic strength = 1.5.

<table>
<thead>
<tr>
<th>$((\text{IO}_3^-)/(\text{Fe(II)})_o$</th>
<th>(Fe(II))$_o$</th>
<th>(IO$_3^-$)$_o$</th>
<th>(H$^+$)$_o$</th>
<th>$k_p \times 10^5$ (s$^{-1}$)</th>
<th>$k \times 10^3$ (M$^{-1}$s$^{-1}$)</th>
<th>$k' \times 10^3$ (M$^{-2}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>.00292</td>
<td>.0225</td>
<td>1.13</td>
<td>2.62</td>
<td>1.22</td>
<td>1.08</td>
</tr>
<tr>
<td>12</td>
<td>.00281</td>
<td>.0342</td>
<td>1.13</td>
<td>3.90</td>
<td>1.09</td>
<td>0.97</td>
</tr>
<tr>
<td>66</td>
<td>.00078</td>
<td>.0515</td>
<td>1.43</td>
<td>7.72</td>
<td>1.46</td>
<td>1.02</td>
</tr>
<tr>
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<td>.0444</td>
<td>1.11</td>
<td>5.02</td>
<td>1.11</td>
<td>1.00</td>
</tr>
<tr>
<td>72</td>
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<td>.0487</td>
<td>.556</td>
<td>2.75</td>
<td>0.51</td>
<td>0.91</td>
</tr>
<tr>
<td>74</td>
<td>.00058</td>
<td>.0429</td>
<td>1.39</td>
<td>6.60</td>
<td>1.60</td>
<td>1.15</td>
</tr>
<tr>
<td>78</td>
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<td>.0493</td>
<td>.867</td>
<td>4.58</td>
<td>0.92</td>
<td>1.06</td>
</tr>
<tr>
<td>78</td>
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<td>.0493</td>
<td>.867</td>
<td>4.30</td>
<td>0.90</td>
<td>1.04</td>
</tr>
<tr>
<td>79</td>
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<td>7.00</td>
<td>1.29</td>
<td>1.12</td>
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<tr>
<td>82</td>
<td>.00065</td>
<td>.0534</td>
<td>1.16</td>
<td>7.20</td>
<td>1.32</td>
<td>1.15</td>
</tr>
<tr>
<td>84</td>
<td>.00060</td>
<td>.0502</td>
<td>.572</td>
<td>2.75</td>
<td>0.52</td>
<td>0.91</td>
</tr>
<tr>
<td>85</td>
<td>.00062</td>
<td>.0525</td>
<td>.834</td>
<td>4.40</td>
<td>0.85</td>
<td>1.02</td>
</tr>
</tbody>
</table>
TABLE V.

Continued........

<table>
<thead>
<tr>
<th>((IO₃⁻)/(Fe(II)))₀</th>
<th>(Fe(II))₀</th>
<th>(IO₃⁻)₀</th>
<th>(H⁺)₀</th>
<th>kₚ x10⁵(s⁻¹)</th>
<th>k x10³(M⁻³s⁻¹)</th>
<th>k' x10³(M⁻²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>0.00075</td>
<td>0.0708</td>
<td>0.578</td>
<td>4.74</td>
<td>0.67</td>
<td>1.16</td>
</tr>
<tr>
<td>94</td>
<td>0.00078</td>
<td>0.0708</td>
<td>0.578</td>
<td>4.77</td>
<td>0.68</td>
<td>1.18</td>
</tr>
<tr>
<td>99</td>
<td>0.00051</td>
<td>0.0505</td>
<td>1.11</td>
<td>6.07</td>
<td>1.18</td>
<td>1.06</td>
</tr>
<tr>
<td>111</td>
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<td>0.0564</td>
<td>1.11</td>
<td>5.97</td>
<td>1.04</td>
<td>0.93</td>
</tr>
<tr>
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<td>0.00040</td>
<td>0.0457</td>
<td>1.44</td>
<td>7.53</td>
<td>1.66</td>
<td>1.15</td>
</tr>
<tr>
<td>114</td>
<td>0.00040</td>
<td>0.0457</td>
<td>1.44</td>
<td>7.52</td>
<td>1.56</td>
<td>1.08</td>
</tr>
<tr>
<td>208</td>
<td>0.00028</td>
<td>0.0583</td>
<td>0.858</td>
<td>5.32</td>
<td>0.90</td>
<td>1.05</td>
</tr>
<tr>
<td>52</td>
<td>0.00110</td>
<td>0.0584</td>
<td>0.896</td>
<td>5.38</td>
<td>0.92</td>
<td>1.03</td>
</tr>
<tr>
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<td>0.0436</td>
<td>1.14</td>
<td>5.00</td>
<td>1.15</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Mean k' = 1.05(±0.07)x10⁻³ M⁻²s⁻¹
Figure (12) : Plot of ln(k) versus ln((H\(^+\)_\(_0\)).

The least squares slope of the line through the data is the order in acid. Data points at acid concentrations below 0.50 M have been neglected in the determination. Temperature = 30.0 \(\pm\) 0.2 °C, ionic strength = 1.5.
all runs in which the acid concentration is accurately known is $1.05 \pm 0.07 \times 10^{-3} \text{ M}^{-2} \text{ sec}^{-1}$.

Below an acid concentration of 0.556 M our rate data becomes inconsistent and irreproducible. These problems result from the precipitation of ferric iodate, Fe(IO$_3$)$_3$, which seems to be favored at low pH. All runs at acid concentrations below 0.556 M resulted in the formation of ferric iodate.

Initiation of reaction (1) undoubtedly involves an equilibrium between iodate, hydrogen-ion, and iodic acid. In the pH range within which the first order acid dependence holds almost all iodate is complexed as iodic acid, therefore the iodic acid equilibrium cannot be responsible for the first order acid dependence. At lower acidities the order in acid must rise to values approaching two as the iodic acid equilibrium becomes important. This conclusion is supported by figure (6) which shows a rise in initial acid order at low acid concentrations. The form of the rate law at low acidities is most likely:

$$ (56) \ - \ \frac{1}{10} \ \frac{\delta (\text{Fe(II))}}{\delta t} = \text{krate} \ (H^+)^2 \ (\text{Fe(II)}) \ (\text{IO}_3^-) $$

Equation (56) applies to runs at low acidities in which iodine is extracted.

**d. Perchlorate-ion dependence**

Myers' and Kennedy's observations that the rate of exchange of iodine atoms between iodate and molecular
iodine depends on the perchlorate-ion concentration raises the possibility of a perchlorate-ion dependence on the rate of reaction (1). Table (VI) compares the rate constant $k'$ measured for two runs. Run number (1) is run at an ionic strength of 0.90 and a perchlorate-ion concentration of 0.90 M. Run (2) is identical to run (1) except that the ionic strength is now 1.50 and the perchlorate-ion concentration is 1.50 M. $k'$ for runs (1) and (2) are essentially identical, any differences probably arising from ionic strength differences. Therefore, the rate of reaction (1) is independent of the perchlorate-ion concentration for experiments in which iodine is continuously extracted from the reaction medium.

3. Iodine Accumulation Experiments

Three iodine accumulation runs were carried out. These runs span a range of $((\text{IO}_3^-)/(\text{Fe(II)})_0$ from 2.5 to 11.8. These experiments are important to the development of a mechanism for reaction (1) by numerical simulation.

Figure (13) is a plot of two kinetic runs, identical in all respects except that in one iodine accumulates in the reaction medium while in the other it is continuously extracted from the reaction medium. This plot clearly shows the accelerating effect iodine has on the reaction rate as well as the characteristic S-shape of autocatalytic data.
TABLE VI.

The effect of perchlorate-ion concentration on the rate constant of equation (55). Iodine was continuously extracted from the reaction medium for each of these runs. The ionic strength is 0.90 for run #1 and 1.50 for run #2. Temperature = 30.0 ± 0.2°C.

\[(\text{Fe}^{(II)})_o = 0.011 \text{ M}\]
\[(\text{IO}_3^-)_o = 0.0584 \text{ M}\]
\[(\text{H}^+)_o = 0.90 \text{ M}\]

<table>
<thead>
<tr>
<th>RUN</th>
<th>((\text{ClO}_4^-)_o)</th>
<th>(k' \times 10^3 \text{ M}^{-2} \text{ sec}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.90 M</td>
<td>0.968</td>
</tr>
<tr>
<td>2</td>
<td>1.50 M</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Figure (13): Plot of two identical kinetic runs except that iodine was continuously extracted from the reaction medium for the run resulting in the linear plot, while it was allowed to accumulate for the run resulting in the curved plot.
B. DISCUSSION

A mechanism for reaction (1) is now proposed. All conceivably important elementary steps that may lead to reaction are considered. When possible a discussion of pertinent rate data from the literature is presented, and rate constants are assigned to elementary processes. In the numerical simulation division of this section the procedure used in evaluating the importance of elementary steps to the mechanism is discussed. Any mechanism put forth for the oxidation must explain all experimental facts.

1. First mechanistic proposal

The first mechanistic proposal consists of the following elementary processes:

\[ (57) \ H^+ + IO_3^- \rightleftharpoons K_{57} \ HIO_3 \]

\[ (58) \ HIO_3 + H^+ \rightleftharpoons K_{58} \ H_2^+IO_3 \]

\[ (59) \ H_2^+IO_3 + Fe(II) \xrightarrow{K_{59}} IO_2 + H_2O + Fe(III) \ (rate \ limiting) \]

\[ (60) \ IO_2 + Fe(II) + H^+ \rightarrow HOIO + Fe(III) \]

\[ (61) \ HOIO + Fe(II) + H^+ \rightarrow IO + Fe(III) + H_2O \]

\[ (62) \ IO + Fe(II) + H^+ \rightarrow HOI + Fe(III) \]

\[ (63) \ HOI + Fe(II) + H^+ \rightarrow \frac{1}{2}I_2 + Fe(III) + H_2O \]
(64) $\text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOI} + \text{I}^- + \text{H}^+$

(65) $\text{HOIO} + \text{I}^- + \text{H}^+ \rightleftharpoons 2\text{HOI}$

(66) $\text{IO}_3^- + \text{HOIO} + \text{H}^+ \rightleftharpoons 2\text{IO}_2 + \text{H}_2\text{O}$

(67) $2\text{HOIO} \rightleftharpoons \text{IO}_3^- + \text{HOI} + \text{H}^+$

(68) $\text{IO}_3^- + \text{I}^- + 2\text{H}^+ \rightleftharpoons \text{HOIO} + \text{HOI}$

All chemical species of the mechanism are understood to exist in aqueous media. The species $\text{I}^-$, $\text{HOI}$, $\text{I}_2$, and $\text{IO}_3^-$ are known to exist in aqueous media, and these species are likely involved in the mechanism of reaction (1). Amichai and Treinin\(^\text{17}\) have shown the existence of $\text{I}_2$ and $\text{IO}_2$ radicals in flash photolysis studies of aqueous NaIO and NaIO\(_3\) solutions. No direct evidence suggesting the existence of HOIO or $\text{H}_2^+\text{IO}_3$ in aqueous media is available.

The existence of only the monomeric species $\text{IO}_3^-$, $\text{HIO}_3$, $\text{H}_2^+\text{IO}_3$, $\text{IO}_2$, HOIO, IO, HOI, $\text{I}^-$, and dimeric species $\text{I}_2$ are recognized in the mechanism. These oxyiodine compounds are likely important to the kinetics of reaction (1) because elementary processes involving the analogous oxybromine species have been shown to be important in explaining the kinetics of many oxybromine systems.\(^\text{18}\)

Dimeric species such as $\text{H}_2\text{I}_2\text{O}_6$ and $\text{H}_2\text{I}_2\text{O}_3$ are not considered in the mechanism although Furuichi and Liebhafsky\(^\text{9}\) suggest them as intermediates in the Dushman Reaction and Liebhafsky and Wu\(^\text{19}\) suggest them as intermediates in their mechanism for the Bray-Liebhafsky
Reaction. No direct evidence suggesting the existence of dimeric oxyiodine intermediates is available, and we do not need to invoke them in order to explain the kinetics of reaction (1).

We assume that proton exchange to and from oxygen and iodine is extremely rapid, and therefore all steps of the mechanism are bimolecular. For instance, step (63) may be written either as:

(69) \[ \text{HOI} + \text{H}^+ \rightleftharpoons \text{H}_2^+\text{OI} \]
(70) \[ \text{H}_2^+\text{OI} + \text{Fe(II)} \rightarrow \frac{3}{2}\text{I}_2 + \text{Fe(III)} + \text{H}_2\text{O} \]

or as,

(71) \[ \text{HOI} + \text{Fe(II)} \rightarrow \frac{3}{2}\text{I}_2 + \text{Fe(III)} + \text{OH}^- \]
(72) \[ \text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} \]

All steps of the mechanism can therefore be written as a series of bimolecular elementary processes.

The first two steps of the mechanism are equilibria involving successive protonations of iodate. Assuming that steps (57) and (58) are at equilibrium, that step (59) is rate limiting, and that the remaining steps are rapid, the following rate law is predicted by the mechanism:

(73) \[ -\frac{1}{10} \frac{\delta (\text{Fe(II)})}{\delta t} = \frac{k_{59}K_{57}^3K_{58}^2 (\text{I}^3^-) (\text{H}^+)^2 (\text{Fe(II)})}{[1 + K_{57} (\text{H}^+)] [1 + K_{58} (\text{H}^+)]} \]

where \( k_{59} \) is the rate constant for step (59), and \( K_{57} \) and \( K_{58} \) are equilibrium constants for steps (57) and (58) respectively. In the derivation of equation (73) steps
involving $I_2$ are ignored, and it therefore applies only to iodine extraction experiments. Assuming $K_{58}$ ($H^+$) to be small compared to one, $K_{57}$ ($H^+$) will dominate the denominator of equation (73) at high acidities. Therefore, at high acidities a first order acid dependence should prevail, just as found experimentally. At lower acidities, $K_{57}$ ($H^+$) becomes less important and the acid dependence should rise. These limiting forms for the rate laws are given in equations (74) and (75).

\[
(74) \quad -\frac{1}{10} \frac{\delta(\text{Fe(II)})}{\delta t} = k_{57}K_{56}(H^+)(IO_3^-)(\text{Fe(II)})
\]  
\text{(High acidities)}

\[
(75) \quad -\frac{1}{10} \frac{\delta(\text{Fe(II)})}{\delta t} = k_{57}K_{56}K_{55}(H^+)^2(IO_3^-)(\text{Fe(II)})
\]  
\text{(Low acidities)}

In equation (73) $K_{56}$ must be small or else zeroth order dependence on acid will occur at high acidities, something that is not observed experimentally.

Step (57) is an equilibrium between iodate and iodic acid. At 30°C its equilibrium constant is 5.75 M\(^{-1}\). Assuming the protonation of iodate is diffusion controlled, a value of $1 \times 10^{10}$ M\(^{-1}\) sec\(^{-1}\) can be assigned to $k_{57}$. On the basis of $K_{57} = 5.75$ M\(^{-1}\), the reverse reaction must have a rate constant, $k_{57}$, of $1.74 \times 10^9$ sec\(^{-1}\).

Step (58) is the reversible protonation of iodic acid. This equilibrium has been postulated as being important in the mechanism of both the iodine-iodate
exchange reaction and the Dushman Reaction. Both investigations postulate an acid induced dissociation of iodic acid into water and $\text{IO}_2^+$, as in equation (76).

\[
(76) \quad \text{HIO}_3 + \text{H}^+ \rightleftharpoons \text{IO}_2^+ + \text{H}_2\text{O}
\]

Neither account reports an equilibrium constant for equation (76). Equations (58) and (76) are essentially identical, and it cannot be determined kinetically whether $\text{IO}_2^+$ or $\text{H}_2^+\text{IO}_3$ is involved in the equilibrium. The equilibrium constant for step (58) must be chosen sufficiently small to insure that the mechanism doesn't predict zeroth order acid dependence at high acidities. $K_{58}$ is chosen as 0.1 M$^{-1}$ to circumvent this problem.

The rate limiting step for kinetic runs in which iodine is continuously extracted from the reaction medium is step (59). Based on the value of 0.1 M$^{-1}$ chosen for $K_{58}$ and 0.00105 M$^{-2}$ sec$^{-1}$ found for the experimental rate constant $k'$ a value for $k_{59}$ of 0.026 M$^{-1}$ sec$^{-1}$ is required to describe experiments in the acid concentration range 0.556 M to 1.44 M. Of course this value for $k_{59}$ depends on the value chosen for the equilibrium constant of step (58), if $K_{58}$ is lowered $k_{59}$ would have to be increased.

Steps (60) thru (63) are successive, irreversible one-electron oxidations of ferrous-ion by unstable oxyiodine intermediates leading to the production of iodine. Compared to step (59) all of these one-electron transfers are rapid. A feeling for their rapidity is
gained by consideration of the rate constant for the oxidation of cerium (III) by the bromine dioxide radical:

\[
H^+(aq) + BrO_2(aq) + Ce(III)(aq) \rightarrow Ce(IV)(aq) + HOBrO(aq)
\]

The forward rate constant for reaction (77) at 25°C is estimated to be \(6.5 \times 10^5\) M\(^{-2}\) sec\(^{-1}\). Because oxyiodine compounds are generally more reactive than oxybromine compounds and because ferrous-ion and cerous-ion are both good reducing agents, we expect steps (60) thru (63) to have rate constants ranging somewhere between \(1 \times 10^5\) M\(^{-2}\) sec\(^{-1}\) and a diffusion controlled value of \(1 \times 10^{10}\) M\(^{-2}\) sec\(^{-1}\).

Steps (64) thru (68) all involve oxygen atom transfer between oxyiodine compounds. All of these reactions may contribute to the evolution of reaction (1) in light of the fact that the analogous oxybromine reactions are well characterized. Evidence in favor of the oxybromine analogues of steps (64) through (68) has been reviewed by Field, Köros, and Noyes.\(^{18}\) In addition all of these steps are of importance in the mechanism of the Bray-Liebhafsky reaction proposed by Sharma and Noyes.\(^{13}\) Sharma and Noyes\(^{13}\) have summarized the pertinent rate constant data.

Step (64) is the reversible hydrolysis of iodine. Eigen and Kustin\(^3\) report a forward rate constant for reaction (64) of 2.1 sec\(^{-1}\) and a reverse rate constant of \(3.1 \times 10^{12}\) M\(^{-2}\) sec\(^{-1}\). Both rate constants were reported
for 20°C. Unfortunately no activation parameters for hydrolysis have been reported, so the rate constant values reported at 20°C cannot be corrected to the experimental temperature of 30°C. Step (64) turns out to be the entrance into the autocatalytic production of iodine for the mechanism. Step (68) also turns out to be important to the autocatalytic scheme of the mechanism. At low iodide-ion concentration ($<10^{-8}$ M) it is the rate limiting step of the Dushman Reaction. Since step (64) is the only step leading to the production of iodide, and its equilibrium constant is small, the iodide concentration existing during the course of reaction (1) is small ($<10^{-6}$ M). We assign the rate constants reported by Furuichi and Liebhafsky to step (68). Their values for $k_{68}$ and $k_{-68}$ are $1.43 \times 10^3$ M$^{-3}$ sec$^{-1}$ and $7.53 \times 10^6$ M$^{-1}$ sec$^{-1}$ respectively at 25°C. We choose their values as opposed to those of Abel and Hilferding since theirs were determined most recently. Both workers' values for $k_{68}$ differ by less than a factor of three. Sharma and Noyes also use the Furuichi and Liebhafsky values for $k_{68}$ and $k_{-68}$ in their mechanism of the Bray Liebhafsky Reaction. No values for the rate constants of steps (65), (66), and (67) have been measured experimentally. Sharma and Noyes have estimated values for them. The details of their estimation processes are summarized elsewhere. Briefly, it is argued that the rate constants for these
oxyiodine reactions cannot be much different from those for the analogous oxybromine cases. Their rate constant estimates are somewhat larger than the values reported for the corresponding oxybromine reactions based on the observations that oxyiodine compounds are more reactive. The rate constants for steps (65) thru (67) are summarized in column (2) of Table (VII).

Column (2) of table (VII) is a tabulation of rate constants for the elementary processes in the initial mechanistic proposal.

2. Numerical Simulation of Experiments

In order to validate the mechanism, the system of 11 simultaneous differential equations resulting from it will be solved. These first order, ordinary differential equations describe the rate of change of concentration for the 11 chemical compounds of the mechanism. If the mechanism is to hold any claim to validity it must reproduce all experimental facts upon numerical solution of this system of differential equations. In the process of numerical simulation an assessment of the relative importance of the steps in the mechanism is made and any elementary processes which are unimportant in describing experiment are identified. Rate constants for steps (59) through (63) are estimated in the simulation process, whereas the remaining rate constants are fixed to the values in column (2) of Table (VII).
TABLE VII.

Rate constant values used in the numerical simulation of the experimental results based on the proposed mechanism.

* Units on the rate constants are $M^{-(N-1)} \text{sec}^{-1}$ where $N$ is the molecularity of the step in question.

<table>
<thead>
<tr>
<th>COLUMN 1</th>
<th>COLUMN 2</th>
<th>COLUMN 3</th>
<th>COLUMN 4</th>
</tr>
</thead>
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<tr>
<td>rate constants</td>
<td>initial rate constant values *</td>
<td>final rate constant values *</td>
<td>temperature (°C)</td>
</tr>
<tr>
<td>$k_{57}$</td>
<td>1.0x10$^{10}$</td>
<td>1.0x10$^{10}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{-57}$</td>
<td>1.74x10$^{9}$</td>
<td>1.74x10$^{9}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{58}$</td>
<td>1.0x10$^{2}$</td>
<td>1.0x10$^{2}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{-58}$</td>
<td>1.0x10$^{3}$</td>
<td>1.0x10$^{3}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{59}$</td>
<td>.024 - .028</td>
<td>.026</td>
<td>30</td>
</tr>
<tr>
<td>$k_{60}$</td>
<td>1.0x10$^{5}$ - 1.0x10$^{10}$</td>
<td>1.0x10$^{5}$ - 1.0x10$^{10}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{61}$</td>
<td>&quot; &quot; &quot;</td>
<td>6.0x10$^{6}$ - 1.0x10$^{10}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{62}$</td>
<td>&quot; &quot; &quot;</td>
<td>1.0x10$^{5}$ - 1.0x10$^{10}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{63}$</td>
<td>&quot; &quot; &quot;</td>
<td>7.0x10$^{4}$</td>
<td>30</td>
</tr>
<tr>
<td>$k_{64}$</td>
<td>2.1</td>
<td>2.1</td>
<td>20</td>
</tr>
<tr>
<td>$k_{-64}$</td>
<td>3.1x10$^{12}$</td>
<td>3.1x10$^{12}$</td>
<td>20</td>
</tr>
<tr>
<td>$k_{65}$</td>
<td>2.0x10$^{10}$</td>
<td>---</td>
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</tr>
<tr>
<td>$k_{-65}$</td>
<td>1.44x10$^{-3}$</td>
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<td>25</td>
</tr>
<tr>
<td>$k_{66}$</td>
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<td>---</td>
<td>25</td>
</tr>
<tr>
<td>$k_{-66}$</td>
<td>1.67x10$^{8}$</td>
<td>---</td>
<td>25</td>
</tr>
<tr>
<td>$k_{67}$</td>
<td>1.0x10$^{9}$</td>
<td>---</td>
<td>25</td>
</tr>
<tr>
<td>$k_{68}$</td>
<td>1.43x10$^{3}$</td>
<td>1.43x10$^{3}$</td>
<td>25</td>
</tr>
<tr>
<td>$k_{-68}$</td>
<td>7.53x10$^{6}$</td>
<td>7.53x10$^{6}$</td>
<td>25</td>
</tr>
</tbody>
</table>
a. Iodine extraction experiments

The initial objective of the simulation consists of reproducing the experimental rate constant \( k' = 1.05 + 0.07 \times 10^{-3} \text{ M}^{-2} \text{ sec}^{-1} \) for experiments in which iodine is continuously extracted from the reaction medium. We simulated the extraction experiments first since they are the least complicated. In order to accomplish simulation the rate constants for steps (64) through (68) are initially set to zero, thus eliminating any path for autocatalysis. A value for \( k_{57} \) of \(0.026 \text{ M}^{-1} \text{ sec}^{-1} \) gives good fit to the experimental data. Table (VIII) compares the experimental rate constant with the rate constant derived from numerical simulation at a number of initial conditions. Values chosen for \( k_{60} \) through \( k_{63} \) do not affect the rate constants derived by simulation if ranged between \(1 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1} \) and \(1 \times 10^{10} \text{ M}^{-2} \text{ sec}^{-1} \). Therefore, as long as the rate constants for steps (60) through (63) are kept above \(1 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1} \), step (59) is rate limiting. The minimum values for \( k_{60} \) through \( k_{63} \) are probably less than \(1 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1} \), but this suspicion was not verified.

Next, values of the rate constants for steps (66) and (67) are inserted since they may be of importance even when iodine is extracted. The rate constants for steps (64), (65), and (68) are maintained at zero. Rates now calculated are much too fast to simulate the experimental
TABLE VIII.

Values of $k'$ calculated by numerical simulation of the iodine extraction experiments. The calculated values of $k'$ are based on the final mechanistic proposal. The experimental value for $k'$ is $1.05 \pm 0.07 \times 10^{-3}\text{ M}^{-2}\text{ sec}^{-1}$.

<table>
<thead>
<tr>
<th>(Fe(II))₀</th>
<th>(IO₃⁻)₀</th>
<th>(H⁺)₀</th>
<th>$k' \times 10^{-3}\text{ M}^{-2}\text{ sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0004 M</td>
<td>0.045 M</td>
<td>1.00 M</td>
<td>1.02</td>
</tr>
<tr>
<td>0.0006</td>
<td>0.05</td>
<td>0.75</td>
<td>0.993</td>
</tr>
<tr>
<td>0.0006</td>
<td>0.045</td>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td>0.0007</td>
<td>0.05</td>
<td>0.50</td>
<td>0.928</td>
</tr>
<tr>
<td>0.0008</td>
<td>0.05</td>
<td>1.50</td>
<td>1.02</td>
</tr>
<tr>
<td>0.003</td>
<td>0.035</td>
<td>1.00</td>
<td>1.01</td>
</tr>
<tr>
<td>0.003</td>
<td>0.020</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.001</td>
<td>0.060</td>
<td>0.75</td>
<td>0.992</td>
</tr>
<tr>
<td>0.025</td>
<td>0.015</td>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td>0.040</td>
<td>0.020</td>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td>0.040</td>
<td>0.020</td>
<td>1.50</td>
<td>1.03</td>
</tr>
<tr>
<td>0.070</td>
<td>0.025</td>
<td>0.50</td>
<td>1.02</td>
</tr>
</tbody>
</table>
results. The acceleration arises from competition between steps (61) and (66) for HOIO.

(61) \[ \text{Fe(II)} + \text{HOIO} + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{IO} + \text{Fe(III)} \]

(66) \[ \text{IO}_3^- + \text{HOIO} + \text{H}^+ \rightarrow 2\text{IO}_2 + \text{H}_2\text{O} \]

In order to eliminate the acceleration, the rate constant for step (61) must be set to at least \(6.0 \times 10^6\). This value for \(k_{61}\) eliminates all competition for HOIO from step (66). With \(k_{61}\) set to \(6.0 \times 10^6\) the experimental rate constants are again reproduced by simulation according to Table (VIII).

If the rate constants for steps (66) and (67) are set to zero, numerical simulation of our extraction experiments is unaffected. Steps (66) and (67) are unimportant to the mechanism of the non-autocatalytic experiments. Additionally, even though \(k_{66}\) and \(k_{67}\) are set to zero, variation of \(k_{62}\), \(k_{63}\), and \(k_{64}\) between \(1 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}\) and \(1 \times 10^{10} \text{ M}^{-2} \text{ sec}^{-1}\) still does not affect the comparison given in Table (VIII).

The mechanism developed to describe the iodine extraction runs (non-autocatalytic experiments) consists of steps (57) through (63) and steps (66) and (67), although the latter two steps are unimportant in simulating experiment. Rate constants for the steps describing the extraction experiments are listed in column (2) of Table (VII). Steps (64), (65), and (68) are non-operative in runs involving iodine extraction.
Numerical simulation of our initial mechanistic proposal for runs involving iodine extraction predicts a second order rate law over the entire range of \([\text{Fe(II)}/(\text{IO}_3^-)]_0\) covered experimentally (equation (76)).

\[
(78) \quad \frac{1}{10} \frac{\delta(\text{Fe(II))}}{\delta t} = k(\text{Fe(II)})(\text{IO}_3^-)
\]

In equation (78) \(k\) depends on the acidity of the reaction mixture. At high initial acid concentrations the rate is first order with respect to acid. At lower initial acid concentrations the order in acid rises to higher values. Figure (14) is a plot of \(\log(k)\) versus \(\log((H^+)_0)\) generated by simulation of the mechanism. At high acid concentrations (greater than 0.5 M) the order in hydrogen-ion is 1.0 while at acid concentrations below 0.5 M this order approaches 1.5 down to an acid concentration of 0.1 M. The dependence of reaction rate on acid concentration predicted by the mechanism parallels that found experimentally, even though it was not possible to do experiments at acidities less than 0.556 M.

b. Iodine accumulation experiments

The second stage of numerical simulation is to reproduce the experimental plots of \((\text{Fe(II)})\) versus time for experiments in which iodine is allowed to accumulate. All the rate constants in column (2) of Table (VII) are now substituted into the differential equation, no rate
Figure (14): A plot of log(k) versus log\((H^+)_o\) generated by numerical solution of the final mechanistic proposal.
constant being set equal to zero. By dropping the rate constant for step (63) to $7.0 \times 10^4$, but keeping $k_{61}$ at $6.0 \times 10^6 \text{ M}^{-2} \text{ sec}^{-1}$ and $k_{60}$ and $k_{62}$ at $1 \times 10^{10}$ we are able to reproduce the experimental results. The simulation is performed for three different $((\ce{IO}_3^-)/\ce{Fe(II)})_0$. Figures (15), (16), and (17) compare the numerically generated plots with the corresponding experimental cases. All three simulations nearly superimpose on the experimental plots. The disparities at low ferrous-ion concentration result from imprecision of the spectrophotometer in measuring low absorbances compared to the essentially exact computational results. The logarithmic plots accentuate the discrepancy.

Variation of $k_{60}$ and $k_{62}$ between $1 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$ and $1 \times 10^{10} \text{ M}^{-2} \text{ sec}^{-1}$ does not affect the form of the simulated plots in figures (15), (16), and (17).

Setting $k_{65}$, $k_{66}$, and $k_{67}$ equal to zero also does not effect the plots in figures (15), (16), and (17). These three steps are of no importance in the mechanism for either the autocatalytic or non-autocatalytic experiments.

Finally, if the rate constants for steps (64) and (68) are set to zero the results of the extraction experiments are still reproduced by numerical simulation as in Table (VIII).
Figure (15): Comparison of the experimental $(\text{Fe(II)})$ versus time data to that generated numerically under identical initial conditions. Temperature $= 30.0 \pm 0.2 \, ^\circ \text{C}$, ionic strength $= 1.5$. 

$(\text{Fe(II)})_0 = 0.028 \, \text{M}$

$(\text{IO}_3^-)_0 = 0.0225 \, \text{M}$

$(\text{H}^+)_0 = 1.13 \, \text{M}$

- ○ experimental
- ■ calculated
Figure (16): Comparison of the experimental (Fe(II)) versus time data to that generated numerically under identical initial conditions.

\[ (\text{Fe(II)})_0 = 0.0029 \, \text{M} \]
\[ (\text{IO}_3^-)_0 = 0.0342 \, \text{M} \]
\[ (\text{H}^+)_0 = 1.13 \, \text{M} \]

- ○ experimental
- □ calculated
Figure (17): Comparison of the experimental (Fe(II)) versus time data to that generated numerically under identical initial conditions. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5.
3. Final Mechanistic Proposal

The rate constants which reproduce all the experimental data for the iodine extraction experiments as well as the iodine accumulation experiments are summarized in column (3) of Table (VII). It must be kept in mind that the rate constants for steps (64) and (68) are for 20°C and 25°C respectively, and not the experimental conditions of 30°C. Nevertheless, the mechanism as developed to this point explains experiment, although $k_{61}$ and $k_{63}$ will change slightly when correct values for $k_{64}$, $k_{-64}$, $k_{68}$, and $k_{-68}$ are used in the simulation.

The following sequence of steps describe experiment:

(57) $H^+ + IO_3^- \rightleftharpoons HIO_3$

(58) $HIO_3 + H^+ \rightleftharpoons H_2^+IO_3$

(59) $H_2^+IO_3 + Fe(II) \longrightarrow IO_2 + H_2O + Fe(III)$

(60) $IO_2 + Fe(II) + H^+ \longrightarrow HOIO + Fe(III)$

(61) $HOIO + Fe(II) + H^+ \longrightarrow IO + Fe(III) + H_2O$

(62) $IO + Fe(II) + H^+ \longrightarrow HOI + Fe(III)$

(63) $HOI + Fe(II) + H^+ \longrightarrow \frac{3}{2}I_2 + H_2O + Fe(III)$

(64) $I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$

(68) $IO_3^- + I^- + 2H^+ \rightleftharpoons HOIO + HOI$

where each step is given the same label as it had in the first mechanistic proposal. Processes (65), (66), and
(67) have been eliminated in the final version of the mechanism.

Steps (57) through (63) correspond to the mechanism of reaction when autocatalysis is suppressed (iodine extraction). The sum of steps (57) through (63) gives to overall stoichiometry of reaction (1).

Process (64) is the entrance into the autocatalytic sequence of the mechanism. Iodine produced by the non-autocatalytic scheme (steps (57) through (63)) is hydrolyzed by step (64) into iodide-ion and hypoiodous acid. Iodide formed by step (64) then reacts with iodate to produce iodous acid and more hypoiodous acid. Hypoiodous acid and iodous acid generated by steps (64) and (68) reacts with more Fe(II) in steps (61) and (63) to produce more iodine. The net result of autocatalysis is the production of 3/2 mole of iodine molecules for every mole of iodine molecules entering the autocatalysis scheme initiated by step (64). The stoichiometry of reaction (1) is generated by the following combination of steps when autocatalysis is operative in the system:

\[(79) \ (61) + (62) + 3(63) + (64) + (68)\]

where the parenthesized numbers refer to steps of the final mechanism.

Table (IX) lists the ranges of concentration of the various oxyiodine intermediates during reactions in which iodine accumulates. These concentration ranges are those
Concentration ranges of intermediate species calculated by numerical solution of the final mechanistic proposal. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5. Calculated values are for iodine accumulation experiments.

### Run #1

- \((\text{Fe(II)})_0 = 0.0808 \text{ M}\)
- \((\text{IO}_3^-)_0 = 0.0137 \text{ M}\)
- \((\text{H}^+)_0 = 1.00 \text{ M}\)
- \((\text{I}_2)_0 = 0.00 \text{ M}\)

### Run #2

- \((\text{Fe(II)})_0 = 0.00028 \text{ M}\)
- \((\text{IO}_3^-)_0 = 0.0583 \text{ M}\)
- \((\text{H}^+)_0 = 1.00 \text{ M}\)
- \((\text{I}_2)_0 = 0.00 \text{ M}\)

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>CONCENTRATION RANGE M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RUN 1</td>
</tr>
<tr>
<td>(\text{I}_2)</td>
<td>(1.56 \times 10^{-3} - 6.40 \times 10^{-3})</td>
</tr>
<tr>
<td>(\text{HIO}_3)</td>
<td>(8.30 \times 10^{-3} - 6.77 \times 10^{-4})</td>
</tr>
<tr>
<td>(\text{H}_2\text{IO}_3)</td>
<td>(8.30 \times 10^{-4} - 6.77 \times 10^{-5})</td>
</tr>
<tr>
<td>(\text{IO}_2)</td>
<td>(2.16 \times 10^{-15} - 1.76 \times 10^{-16})</td>
</tr>
<tr>
<td>(\text{HOIO})</td>
<td>(7.33 \times 10^{-12} - 3.22 \times 10^{-12})</td>
</tr>
<tr>
<td>(\text{IO})</td>
<td>(4.40 \times 10^{-15} - 1.93 \times 10^{-15})</td>
</tr>
<tr>
<td>(\text{HOI})</td>
<td>(1.39 \times 10^{-9} - 1.55 \times 10^{-8})</td>
</tr>
<tr>
<td>(\text{I}^-)</td>
<td>(7.60 \times 10^{-7} - 2.80 \times 10^{-6})</td>
</tr>
</tbody>
</table>
when reaction is between 20% and 80% complete. Entries of the Table are derived by numerical solution of the final mechanism using the rate constants listed in column (3) of Table (VII). Concentration ranges are listed for two simulated runs at different \( \frac{([\text{Fe(II)}])}{([\text{I}^-_3])_0} \), the value 208 being an upper bound to the experimental range of \( \frac{([\text{Fe(II)}])}{([\text{I}^-_3])_0} \) and 0.17 a lower bound to that same range. Both simulated runs are for an initial acid concentration of 1.0 M. At any given time during the course of runs in which iodine accumulates the concentration of the respective oxyiodine intermediates will fall within the ranges given in Table (IX).

Table (X) is strictly analogous to Table (IX) with the exception that the concentration ranges now listed are for runs in which iodine is extracted from the reaction mixture. In arriving at the values of Table (X) by numerical solution of the final mechanism, \( k_{64} \) and \( k_{68} \) are set to zero in order to eliminate autocatalysis.

Table (IX) shows that the concentration of iodide is always less than \( 10^{-5} \) M for runs in which iodine is allowed to accumulate. This low value for the iodide concentration is reasonable since the only source of iodide is step (64) (iodine hydrolysis) which has an extremely small equilibrium constant. Any iodide produced by hydrolysis is rapidly scavenged by iodate in step (68) resulting in low iodide steady state.
Concentration ranges of intermediate species calculated by numerical solution of the final mechanistic proposal. Calculated values are for iodine extraction experiments. Temperature = 30.0 ± 0.2 °C, ionic strength = 1.5.

Run #1
(Fe(II))₀ = 0.0808 M
(IO₃⁻)₀ = 0.0137 M
(H⁺)₀ = 1.00 M

Run #2
(Fe(II))₀ = 0.00028 M
(IO₃⁻)₀ = 0.0583 M
(H⁺)₀ = 1.00 M

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>CONCENTRATION RANGE M</th>
<th>RUN 1</th>
<th>RUN 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIO₃</td>
<td>8.06x10⁻³ - 3.97x10⁻³</td>
<td></td>
<td>4.58x10⁻² - 4.57x10⁻²</td>
</tr>
<tr>
<td>H₂IO₃</td>
<td>8.06x10⁻⁴ - 3.97x10⁻⁴</td>
<td></td>
<td>4.58x10⁻³ - 4.57x10⁻³</td>
</tr>
<tr>
<td>IO₂</td>
<td>2.10x10⁻¹⁵ - 1.03x10⁻¹⁵</td>
<td>2.97x10⁻¹⁴ - 2.03x1⁻¹⁰</td>
<td></td>
</tr>
<tr>
<td>HOIO</td>
<td>3.49x10⁻¹² - 1.72x10⁻¹²</td>
<td>3.46x10⁻¹¹ - 1.04x10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>IO</td>
<td>2.10x10⁻¹⁵ - 1.03x10⁻¹⁵</td>
<td>2.08x10⁻¹⁴ - 6.25x10⁻¹¹</td>
<td></td>
</tr>
<tr>
<td>HOI</td>
<td>2.99x10⁻¹⁰ - 1.48x10⁻¹⁰</td>
<td>2.97x10⁻⁹ - 4.46x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>I⁻</td>
<td>1.85x10⁻²¹ - 8.42x10⁻²¹</td>
<td>1.83x10⁻²⁰ - 1.17x10⁻¹⁷</td>
<td></td>
</tr>
</tbody>
</table>
concentrations. These low iodide concentrations correspond to those of Furuichi and Liebhafsky in their investigation of the Dushman Reaction.

The concentration of iodide is always nearly zero for kinetic runs in which iodine is continuously extracted from the reaction medium, since the only major source of iodide is iodine hydrolysis.

Close examination of the results of numerical solution of the differential equations resulting from the final mechanism indicate that steps (57), (58), and (64) are all near equilibrium. These numerical solutions also show that step (68) is essentially irreversible.

4. Numerical Simulation of the Initial Rate Experiments

As a final check on the validity of the mechanism the initial rate studies were numerically simulated. The procedure for analyzing initial rate data generated by computer simulation is identical to that used for the experimental data. Simulation is performed for the same initial conditions as the corresponding experiments. If the mechanism is plausible it should reproduce the initial orders in all principal reactant species, both when iodine is initially present in the reaction medium as well as when it is not.

Table (XI) lists the initial orders generated by simulation for Fe(II), IO\textsubscript{3}\textsuperscript{-}, and H\textsuperscript{+}. This table also
makes a comparison between the initial orders predicted from numerical solution of the mechanism and the experimental initial orders. For all three reactants agreement between simulation and experiment is good. An initial order of $1.10 \pm 0.02$ in Fe(II) agrees well with the value $1.15 \pm 0.02$ found experimentally. Prediction of this non-integral order greater than one is excellent evidence in favor of the final mechanistic proposal.

The initial iodine dependence is also reproduced well by simulation of the mechanism. Figure (18) is a log-log plot of the initial iodine dependence predicted by the mechanism. This plot has a definite curvature to it, but an initial order in iodine of between 0.14 and 0.19 can be estimated from it. This range of values encompasses the experimental initial order in iodine of $0.15 \pm 0.02$. The mechanism correctly predicts an acceleration of initial rate by added iodine. Table (XI) compares the experimental and simulated initial iodine orders.

Experimentally the initial orders in both iodate and ferrous-ion decrease when iodine is present initially in the reaction medium as opposed to when it is not. Numerical simulation successfully predicts this drop in initial order for these two species. The results of these simulations are given in Table (XI). Although the drop in order is not quantitatively predicted by the mechanism, the lowering trend is still present.
Comparison of initial orders generated by experiment and numerical simulation. No error estimates have been made for some of these orders. Temperature = 30.0 ± 0.4 °C, ionic strength = 1.5.

<table>
<thead>
<tr>
<th>REACTANT SPECIES</th>
<th>INITIAL IODINE CONCENTRATION M</th>
<th>INITIAL ORDERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>0.0</td>
<td>1.15 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>3.0 x 10^-4</td>
<td>0.94</td>
</tr>
<tr>
<td>IO_3^-</td>
<td>0.0</td>
<td>0.98 ± 0.02</td>
</tr>
<tr>
<td>IO_3^-</td>
<td>1.5 x 10^-4</td>
<td>0.89</td>
</tr>
<tr>
<td>H^+</td>
<td>0.0</td>
<td>1.00 ± 0.03</td>
</tr>
<tr>
<td>I_2</td>
<td>3.0 x 10^-5 - 1.5 x 10^-4</td>
<td>0.15 ± 0.02</td>
</tr>
</tbody>
</table>
(Fe(II))₀ = 0.0727 M
(IO₃⁻)₀ = 0.004128 M
(H⁺)₀ = 1.00 M
d = 0.16 ± 0.03

Figure (18) : A plot of -log(initial rate) versus -log(I₂)₀ generated by numerical solution of the final mechanistic proposal. The slope of this plot is the initial order in iodine, d.
Not only are experiments involving iodine extraction and accumulation consistent with the final mechanistic proposal, but the initial rates studies are also consistent with it.

5. Suggestions for Further Work

It is impossible to perform every conceivable experiment relating to the kinetics of process (1). In this investigation a variety of experiments covering a broad range of initial conditions have been carried out. Since the proposed mechanism in its final form (steps (57) through (63), (64) and (68)) reproduces all the experimental facts, it is assumed to be correct. However, the possibility cannot be ruled out that future experiments may disprove it.

Experimental determination of a order in hydrogen ion at low acidities for the extraction experiments is important in establishing the validity of the mechanism. The mechanism predicts a first order acid dependence between 0.5 M and 1.5 M acid, and a higher order dependence below 0.5 M. In the high acid concentration range the mechanism as finally developed describes experiment accurately, but at hydrogen-ion concentrations less than 0.556 M an order increase cannot be confirmed. At low
acidities the experimental data are inconsistent, probably the result of interference from ferric iodate precipitating from the reaction medium. Even though it is reasonable that the order in acid should rise to values approaching two at low acidities, this rise should be confirmed experimentally. Low acid studies may be successful under conditions of low initial ferrous-ion concentration and iodate-ion concentrations (both less than .001 M). For these initial conditions Fe(III) and IO₃⁻ will both exist in low concentration in the reaction mixture, and therefore formation of ferric iodate will not be favored.

For runs in which iodine is continuously extracted from the reaction medium, the rate of oxidation of (Fe(II)) is given by equation (55). No rate law is reported for runs involving iodine accumulation. Theoretically it is possible to derive a general rate law from any mechanism by invoking the steady state and equilibrium approximations. In practice such a technique is difficult for complex mechanisms such as that proposed for reaction (1). A general rate law would serve as a convenient summary of experiment, and all experimental observations should be derivable from it.

Another future experiment of interest is resimulation of the experimental data when accurate rate constant values are known for steps (64) and (68). Both these rate constants are in error for reasons given in the
discussion section of this account. When accurate values for these parameters are determined, resimulation will give a correct value for the rate constant of step (63) as well as an accurate lower bound for the value of $k_{61}$. Both of these rate constants were evaluated during computer simulation of the rate data.
CHAPTER IV

SUMMARY

The kinetics of the oxidation of ferrous-ion by iodate-ion in strong perchloric acid media has been investigated. The study was performed at a temperature of 30.0 ± 0.2°C and an ionic strength of 1.5 M. We agree with previous investigators that the reaction is autocatalytic in the production of iodine. The following rate law describes experiments in which iodine is continuously extracted from the reaction medium:

\[
\frac{1}{10} \frac{\delta(\text{Fe(II)})}{\delta t} = k' (\text{Fe(II)}) (\text{IO}_3^-) (H^+)
\]

where \( k' \) has the value \( 1.05 \pm 0.07 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1} \). The first order dependence of the rate on ferrous-ion concentration is in disagreement with other investigators who claim the rate does not depend upon ferrous-ion concentration. Rate law (55) applies only in the hydrogen-ion concentration range between 0.556 M and 1.44 M. At lower acidities simulation of our proposed mechanism indicates that the reaction rate probably becomes second order in acid, as is shown in equation (56).

\[
\frac{1}{10} \frac{\delta(\text{Fe(II)})}{\delta t} = k_{\text{rate}} (\text{Fe(II)}) (\text{IO}_3^-) (H^+)^2
\]

Initial reaction rate is described by equation (47).
Equation (47) holds only when no iodine is present in the reaction medium initially. The initial order in iodine is $0.15 \pm 0.02$. When iodine is initially present in the reaction mixture the orders in ferrous-ion and iodate drop significantly below the orders found in the absence of an initial iodine concentration.

Equations (55) through (61) and equations (62) and (66) are proposed as steps in the mechanism explaining the kinetics of reaction (1). With the values for rate constants listed in column (3) of Table (VII), computer simulation of the proposed mechanism reproduces the results of experiment. No general rate law describing the rate of oxidation is proposed.
REFERENCES

15. Ibid., 761.

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