

Reactions Involving Hydrogen Peroxide, Iodine, and Iodate Ion. 6. Oxidation of Iodine by Hydrogen Peroxide at 50 °C

Herman A. Liebhafsky,* William C. McGavock, Robert J. Reyes, Glenn M. Roe, and Lawrence S. Wu

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843, Trinity University, San Antonio, Texas, School of Aerospace Medicine, Brooks Air Force Base, Texas, Corporate Research and Development, General Electric Co., Schenectady, New York. Received February 18, 1977

Abstract: The oxidation of iodine by hydrogen peroxide has been studied at 50 °C with modern equipment, stopped-flow apparatus included, that gave spectrophotometric records of the rates at which iodine disappeared. A computer was used in the interpretation of the new results, which are greatly improved over those published in 1931. Part of the skeleton mechanism previously postulated for this reaction system was strengthened, part was shown to need modification, and 7.2 min⁻¹ was established as the maximum observable first-order specific rate for the disappearance of iodine at 50 °C. This datum appears to be independent of the concentrations of peroxide, acid, and iodate, and of (the very low) concentrations of iodide.

In 1931, Bray and Liebhafsky (Table I)¹ summarized the results of qualitative experiments that provide a partial overview of the complex and interesting reaction system H₂O₂, I₂, IO₃⁻. To simplify the overview, the omnipresent catalytic decomposition of H₂O₂ was omitted, as were the oxidation-reduction reactions of the many iodine species among themselves.¹⁻⁶ Such reactions, of which the disproportionation of I₂ into IO₃⁻ and I⁻ is an illustrative example,⁷ occur throughout the reaction system. The most interesting region in this system is the triangle outlined by expt *i* (I₂ → IO₃⁻) (II and IV);⁶ expt *m* (IO₃⁻ → I₂) (III);⁶ and expt *k* (IO₃⁻ → I₂ + I⁻) (1928 results as yet unpublished).

Experiment *i* has spawned no end of trouble. HIO₃ can be prepared by the action of H₂O₂ on I₂ (II), but the method suffers owing to the unavoidable, wasteful decomposition of H₂O₂. More important, the experiment has presented chemical kinetics with an enigma unresolved after half a century.

The main features of the enigma are these. H₂O₂ cannot accomplish I₂ → IO₃⁻ unless adequate concentrations of the reaction products H⁺ and IO₃⁻ are present so suppress I⁻ (II and IV). Then the transformation can go quickly and smoothly at a rate that decreases, with [I₂] as the only rational concentration variable; the measured specific rate varies confusingly. In particular, increasing the concentration of H₂O₂, the substance that makes the oxidation possible, decreases its rate—sometimes to zero.

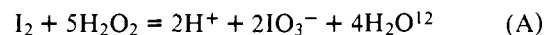
The enigma has a deceptively simple feature—a maximum limiting rate, that is, a maximum value of the specific rate. With [I₂] as the only concentration in the rate law, it was natural to assume that the rate of I₂ hydrolysis set this upper limit. II concludes with “the oxidation of iodine by hydrogen peroxide furnishes a direct way of investigating the hydrolysis of iodine”. The statement was cautiously worded because extensive and convincing prior knowledge was at hand to show that neither I⁻ nor HIO, the only iodineous hydrolysis products, could possibly be oxidized by H₂O₂ at rates comparable with those at which I₂ disappeared in various versions of expt *i*. These misgivings were greatly strengthened by a subsequent kinetic investigation⁸ and became finally overriding in 1962, when the rate of iodine hydrolysis was measured directly⁹ and found to be some 180 min⁻¹ at 20 °C, a value to be compared with 0.6 min⁻¹ at 25 °C, the largest limiting specific rate ever observed in a version of expt *i* (IV). Another mechanism had to be found.

* Author to whom correspondence should be addressed at Texas A&M University.

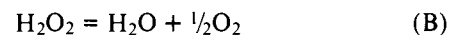
In 1951, thermodynamic evidence was published^{10a} for the “ionic dissociation” of I₂(aq) (into I⁺ and I⁻, both hydrated) at 25 °C, and similar evidence eventually followed^{10b} for 50 °C. Accordingly, it was assumed that the maximum limiting rate in expt *i* was the maximum rate of the ionic dissociation of I₂¹¹ (see also V,⁶ especially footnote 28).

The enormously better equipment available today, and the expectation that results at 50 °C would be simpler than those of II and IV, led to the three investigations summarized here. They deal with the spectrophotometrically recorded rates at which I₂ disappears in experiments related to expt *i*.

In all versions of expt *i*, the stoichiometric reaction



is accompanied by



in varying amounts. Equations A and B take no account of the production or disappearance of the reactive intermediate iodine compounds that make both reactions possible.

Henceforth, we shall describe as UP reactions those in which H₂O₂ raises the oxidation number of an iodine species, and as DOWN reactions, those in which the converse change occurs; DOWN reactions liberate O₂. When the summed UP reactions perfectly balance the summed DOWN reactions, catalysis of H₂O₂ decomposition, reaction B, results. In addition, we must consider the IODINE reactions, so-called because they involve iodine species (e.g., I₂, I⁻, HIO, HIO₂, IO₃⁻) but no H₂O₂. One important function of IODINE reactions is the control of [I⁻] (IV and V).

Iodine Disappearance Measured in Conventional Apparatus (L. S. Wu and H. A. Liebhafsky, experiments completed 1973)

The data in Figures 1, 2, and 3 were obtained by using the apparatus described in V: reaction begins when H₂O₂ is added. The [I₂] values give a variable first-order specific rate, *k*₁₂, defined by

$$-d[I_2]/dt = -R_{I_2} = k_{12}[I_2] \text{ (seconds or minutes)} \quad (C)$$

In each figure, the slopes of the curves approach an upper limit corresponding to 7.2 min⁻¹ (0.12 s⁻¹), represented in each figure by a broken line.

To interpret the new results, we introduce the empirical relation

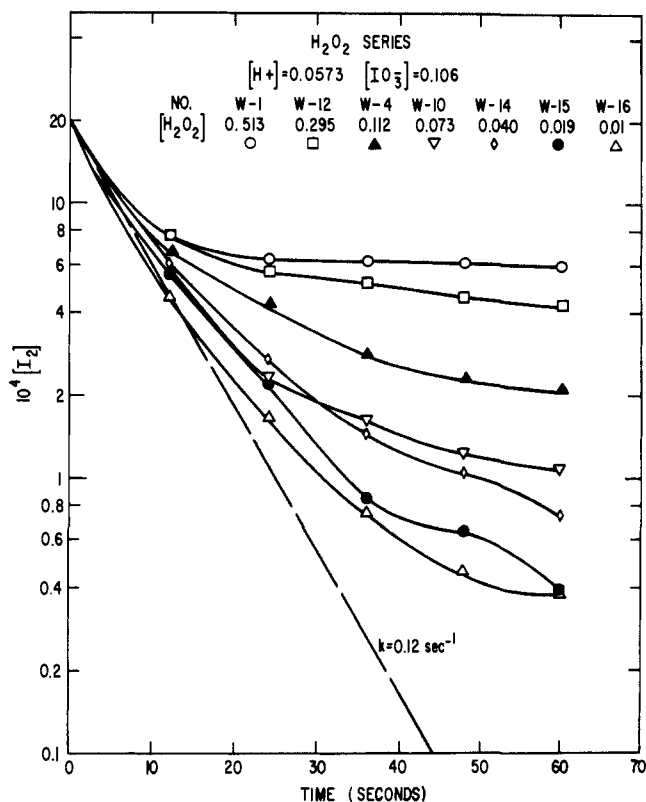


Figure 1. Experiments in conventional equipment. Ordinate is logarithmic. Initial $[I_2]$ calculated from I^- added prior to H_2O_2 addition.

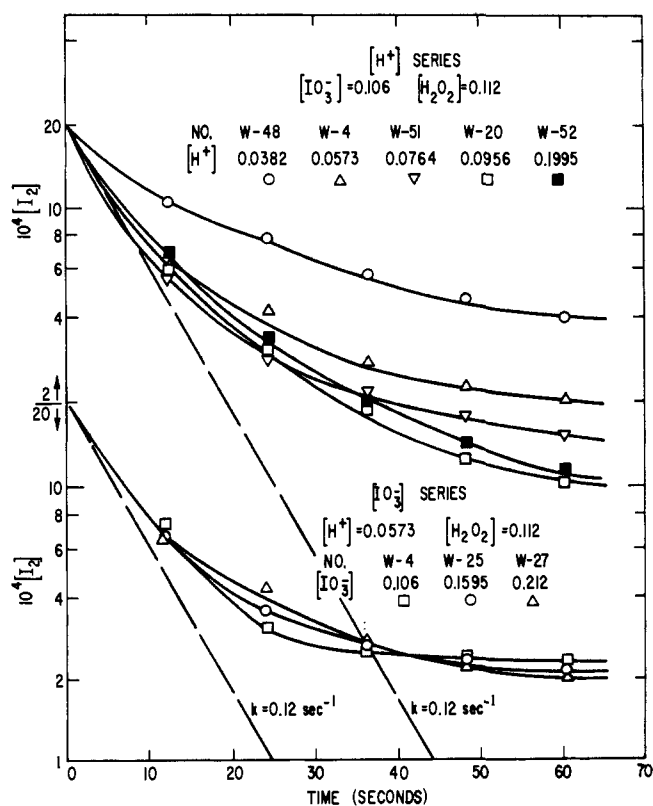


Figure 2. Caption of Figure 1 applies.

$$-R_{I_2} = 7.2[I_2] - F[H_2O_2] \text{ (minutes)} \quad (D)$$

The first term on the right assumes that I_2 disappears in a single UP reaction at a rate independent of $[H_2O_2]$ though H_2O_2 participates in the reaction. The DOWN reactions ap-

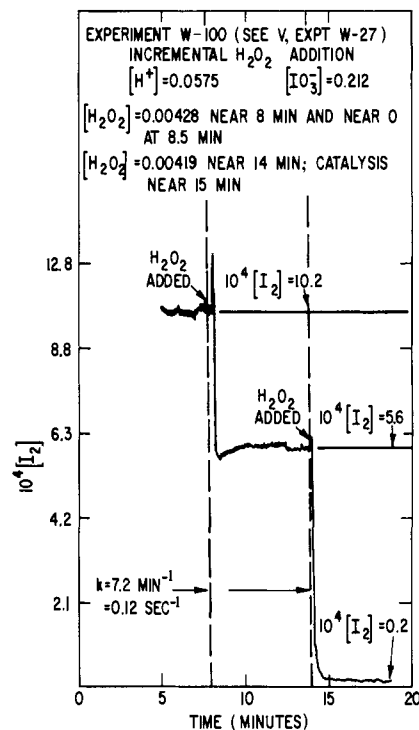


Figure 3. Caption of Figure 1 applies. Incremental H_2O_2 addition used to minimize DOWN reactions.

pear in the second term. The IODINE reactions affect the entire system.

Figures 1 and 2 suggest that 7.2 min^{-1} corresponds to a limiting slope and hence is the *maximum observable* specific rate of the process that limits the rate of the single UP reaction at all the initial concentrations used.

The range of $[I_2]$ values over which the datum 7.2 min^{-1} applies should increase if the $F[H_2O_2]$ term is minimized. In the hope of accomplishing this result, incremental H_2O_2 addition was resorted to in W-100 and other experiments that gave similar results. Reaction B is reduced in importance to where about 1 mL of O_2 was liberated during the disappearance of I_2 ; reaction B thus accounts for some 15% or less of the H_2O_2 added. Comparison with expt 78 (at 0°C) in Figure 1 of IV is of interest. After the first H_2O_2 addition in W-100, there is a small increase in $[I_2]$, considerably less than that in expt 78; both increases are caused by a readjustment in the final concentrations of reactive intermediate iodine species. There is no such increase after the second addition in W-11, probably because reaction B is continuing.¹³

Figure 3 thus provides remarkable confirmation of the basis for eq D; 7.2 min^{-1} is the *maximum observable* first-order specific rate for the disappearance of I_2 . Complete elimination of DOWN reactions, impossible to achieve, would raise 7.2 by a small, indeterminate amount.

Iodine Disappearance in Stopped-Flow Apparatus (R. J. Reyes, W. C. McGavock, and H. A. Liebhafsky, experiments completed 1973)

Experiments resembling those in Figures 1 and 2 were done (at different concentrations) on a Durrum-Gibson stopped-flow apparatus equipped with monochromator, light source, and power supply from a Beckman DU spectrophotometer, the transmitted intensity at 460 nm being recorded with increasing time on a Hewlett-Packard Model 1207B storage scope; the recorded trace was usually photographed.

The stopped-flow equipment was chosen for the additional experiments because it provides superior mixing, because it is better adapted to the study of fast reactions, and because any

oxygen would form in a stagnant reaction mixture under pressure.¹³ One drive syringe contained dissolved I_2 (generated by prior addition of KI), KIO_3 , and $HClO_4$; the other, H_2O_2 and $HClO_4$. There was no change in acid concentration on mixing. Dead time was negligible.

The experimental results are shown in Figures 4 and 5. The concordance with the first two figures is obviously good. Further confirmation of 7.2 min^{-1} was sought in "5-s" experiments on the stopped-flow apparatus, the objective being to obtain a value for this specific rate very soon after thorough mixing. It was found that k_{12} remained constant within the experimental error for 3 s after mixing. The \bar{k} 's, which are the experimental results, are therefore mean specific rates for $t = 1.5 \text{ s}$, or 0.025 min . The datum 7.2 min^{-1} was confirmed under conditions where $F[H_2O_2]$ was expected to be negligible. Detailed results will be given in the computer section to follow.

Comparison of the five new figures with those in IV will show that reasonable order has been achieved where unavoidable disorder was formerly the rule. The new results invite comments under the five headings below.

Concentration of H_2O_2 . According to Figures 1 and 4, $F[H_2O_2]$ in eq D increases systematically with increasing $[H_2O_2]_i$ at constant (but different) values of $[IO_3^-]$ and at constant $[H^+]$. This state of affairs is a great advance over earlier work (especially IV), in which the effect of increasing $[H_2O_2]$ had to be regarded as a mysterious retardation of the oxidation of I_2 by H_2O_2 . Further advance is possible by considering (necessarily imprecise) data for the times (beyond these figures) at which $-R_{I_2} = 0$, $[I_2]_{\min}$ being reached. Then, as is obvious from eq D, $F[H_2O_2]$ and $7.2[I_2]$ should be equal, and, with $[I_2]$ at a minimum, it is safe to consider F constant and to write $[I_2]_{\min}/[H_2O_2] = F/7.2$.

Data for testing this statement are available for the H_2O_2 series of Figure 1. We have

Experiment	W-6 ^a	W-1	W-12	W-4	W-10	W-14	W-15 ^b	W-16 ^b
$10^4[I_2]_{\min}/[H_2O_2]_i$	12	12	14	15	14	13	(11)	(10)

^aExperiment not included in Figure 1 because $[I_2]_{\min}$ was not reached until 19 min, or much later than for the experiments of Figure 1. In W-6, $[H_2O_2]_i$ was 1.0 M; $[H^+]$ and $[IO_3^-]$, as in the figure. High $[H_2O_2]$ makes experiments erratic, probably owing to complexities during mixing: see IV, Table IV, expts 35, 30, and 28, in all of which the final $[H_2O_2]$ was 0.065 (a misprinted value appears for expt 35).

^b Here the decrease in $[H_2O_2]$ must have been appreciable by the time $[I_2]$ reached a minimum. The decrease cannot be calculated. Values of the concentration ratio are sure to be low.

The constancy is satisfactory. In addition, values of this concentration ratio may be calculated for W-24 and W-27 from data in Table I of V. For these experiments, $[H^+] = 0.0572$, $[IO_3^-] = 0.212$ (double that in Figure 1), and $[H_2O_2]_i = 0.112$. For successive pulses in W-24, the ratio is

Pulse	0	1	2	3	4	5	6	7	8
$10^4[I_2]_{\min}/[H_2O_2]$	18	18	20	20	20	19	21	21	22

Clearly, the new results show that the constancy of the concentration ratio found in V for a *succession of pulses* exists also for pulse 0 over a wide range of $[H_2O_2]_i$ values.

This kind of concentration proportionality was found in 1928 during experiments in which H^+ , IO_3^- , and H_2O_2 (but not I_2) were initially present. It has reappeared at other places in V (note especially the sloping straight lines in the figures). This proportionality is one of the most important of all clues to the mechanism of this reaction system. In our view, $F/7.2$ is a constant at $[I_2]_{\min}$ because the rate of the single significant¹⁴ UP reaction (namely, $7.2[I_2]$) is there equal to the sum of the

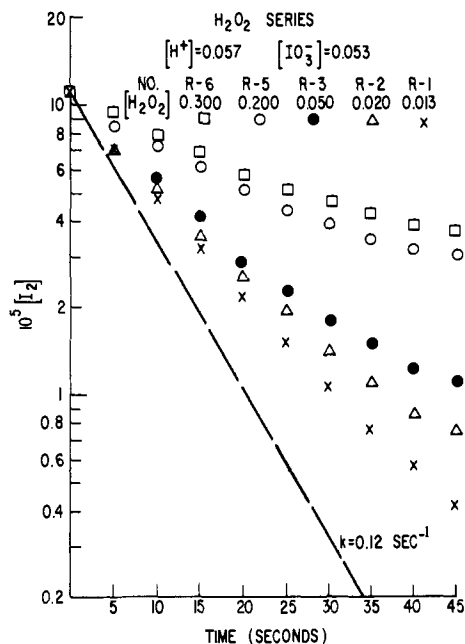


Figure 4. Experiments in stopped-flow apparatus. Ordinate is logarithmic. All $[I_2]$ values from spectrophotometric data via Beer's law.

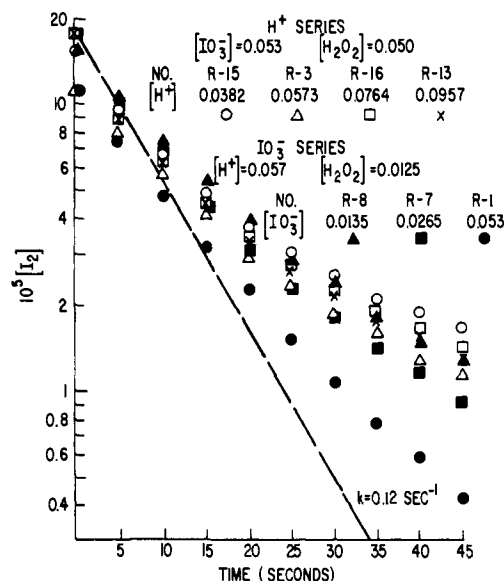


Figure 5. Caption of Figure 4 applies.

rates of all DOWN reactions; reaction B dominates. Exact equality would hold also for $[I_2]_{\max}$ in the oscillatory decomposition (V) and be approached whenever $-R_{I_2}$ is small, as it is during smooth decomposition.

Concentration of H^+ and IO_3^- . The curves of Figures 2 and 5, and the measured values of $[I_2]_{\min}$ to which they lead, show that F (eq D) increases with decreasing $[H^+]$, and increases less quickly with $[IO_3^-]$. The exact functional relationships are not yet known.

Concentration of I^- . The most significant concentration variable, and the most difficult to deal with, is $[I^-]$. This point has been clear for half a century, and it is well illustrated by V (Figure 1 and eq 22).

The new work shows that the datum 7.2 min^{-1} is independent of $[I^-]$. This datum applies both to W-100 (Figure 3), in which $[I^-]$ continued to decrease as I_2 disappeared, and to W-27 (V, Figure 1), for which the reverse was true. Both kinds of variation were confirmed in other experiments. Also, the

Table I. Decrease in $[I_2]$ with Time: Experiment vs. Computer (Figures 1 and 2)

H ₂ O ₂ Series. Experiments W-1 and W-16, Figure 1. $[H^+] = 0.0573$; $[IO_3^-] = 0.106$										
	W-16. $[H_2O_2]_i = 0.010$; $[I_2]_i = 2(10^{-3})$					W-1. $[H_2O_2]_i = 0.513$; $[I_2]_i = 2(10^{-3})$				
$10^4[I_2]$ at ^a	12	24	36	48	60 s	12	24	36	48	60 s
By experiment	4.5	1.65	0.75	0.45	0.32	7.6	6.3	6.2	6.1	6.0
By computer ^b	5.6	2.3	1.27	0.84	0.63	6.7	4.0	3.1	2.7	2.4
By computer: At 0.3 s, $10^4[I_2] = 19.3$ and $k_{I_2} = 7.03 \text{ min}^{-1}$						At 0.3 s, $10^4[I_2] = 19.1$ and $k_{I_2} = 7.18 \text{ min}^{-1}$				
H ⁺ Series. Experiments W-48 and W-52, Figure 2. $[IO_3^-] = 0.106$; $[H_2O_2]_i = 0.112$										
	W-48. $[H^+] = 0.0382$; $[I_2]_i = 2(10^{-3})$					W-52. $[H^+] = 0.1995$; $[I_2]_i = 2(10^{-3})$				
$10^4[I_2]$ at ^a	12	24	36	48	60 s	12	24	36	48	60 s
By experiment	10.5	7.8	5.8	4.8	4.1	6.8	3.4	2.0	1.45	1.15
By computer	5.7	2.6	1.63	1.21	0.98	5.7	2.6	1.63	1.21	0.98
By computer: At 0.3 s, $10^4[I_2] = 19.3$ and $k_{I_2} = 7.24 \text{ min}^{-1}$						At 0.3 s, $10^4[I_2] = 19.2$ and $k_{I_2} = 7.27 \text{ min}^{-1}$				
$[IO_3^-]$ Series. Experiments W-4 and W-27, Figure 2. $[H^+] = 0.0573$; $[H_2O_2]_i = 0.112$										
	W-4. $[IO_3^-] = 0.106$; $[I_2]_i = 2(10^{-3})$					W-27. ^c $[IO_3^-] = 0.212$; $[I_2]_i = 2(10^{-3})$				
$10^4[I_2]$ at ^a	12	24	36	48	60 s	12	24	36	48	60 s
By experiment	6.5	4.3	2.8	2.3	2.1	7.2	3.2	2.6	2.5	2.5
By computer	5.7	2.6	1.6	1.2	0.97	5.7	2.6	1.7	1.24	1.02
By computer: At 0.3 s, $10^4[I_2] = 19.3$ and $k_{I_2} = 7.23 \text{ min}^{-1}$						At 0.3 s, $10^4[I_2] = 19.3$ and $k_{I_2} = 7.24 \text{ min}^{-1}$				

^a Also applicable to experiment on right! ^b Computer data in boldface. ^c See V.

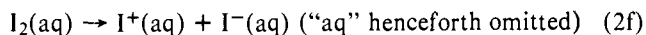
Table II. Specific Rates from "5-sec" Experiments. Experiment versus Computer

H ₂ O ₂ Series: $[H^+] = 0.057$; $[IO_3^-] = 0.053$							
Expt	R-101 ^a	R-102	R-103	R-104	R-105	R-106	
$[H_2O_2]$	0.013	0.025	0.050	0.100	0.200	0.300	
k_{I_2}, min^{-1}	7.2	7.2	5.4	3.6	3.0	2.4	
k_{I_2}, min^{-1}	7.13	7.18	7.19	7.17	7.08	7.02	
First IO_3^- Series: $[H_2O_2] = 0.013$; $[H^+] = 0.057$				Second IO_3^- Series: $[H_2O_2] = 0.100$; $[H^+] = 0.057$			
Expt	R-108	R-107	R-101	R-112	R-111	R-110	R-109
$[IO_3^-]$	0.0135	0.0265	0.0530	0.0070	0.0135	0.0265	0.0835
k_{I_2}, min^{-1}	5.4	7.2	7.2	0.30	0.48	3.6	7.2
k_{I_2}, min^{-1}	7.12	7.13	7.13	7.15	7.17	7.16	7.16
First H ⁺ Series: $[H_2O_2] = 0.050$; $[IO_3^-] = 0.053$				Second H ⁺ Series: $[H_2O_2] = 0.100$; $[IO_3^-] = 0.053$			
Expt	R-115 ^b	R-103	R-114	R-113	R-119	R-118	R-117
$[H^+]$	0.0382	0.057	0.076	0.096	0.0382	0.076	0.096
k_{I_2}, min^{-1}	(6.6)	5.4	6.0	7.2	1.2	3.0	4.2
k_{I_2}, min^{-1}	7.16	7.19	7.19	7.21	7.16	7.18	7.17

^a To avoid confusion with Figures 3 and 4, the identifying number of each "5-s" experiment was increased by 100. ^b In all experiments, $[I_2]$ was near the solubility limit *before* the mixing. In R-115, $[I_2]_i$ (spectrophotometrically determined as were all other values) somewhat exceeded half the solubility of iodine. As $[I_2]_i$ was determined *after* mixing, half the solubility should have been its upper limit. R-115 is best disregarded.

initial $[I^-]$ values differ with the initial values of $[H^+]$, $[I_2]$, $[IO_3^-]$, and $[H_2O_2]$; consequently, the evidence from all experiments that 7.2 min^{-1} is a valid maximum value (see the five figures and Table II) supports the conclusion stated above.

Mechanism of Iodine Disappearance. The most important consequence of the work reported here would be to establish the proposition that the rate of ionic dissociation of aqueous iodine,¹¹ namely,

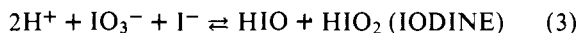
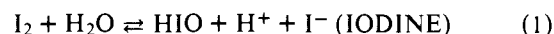


is the *maximum rate* at which the single important UP reaction in our system (the oxidation of I^+ by H_2O_2 ; reaction 4 below) can proceed. The new work supports the following statement: The *maximum observable* specific rate for reaction 2f is 7.2 min^{-1} (perhaps a little more) at 50°C , and this datum is independent of $[H^+]$, $[IO_3^-]$, $[H_2O_2]$, and $[I^-]$ provided $[H^+]$ and $[IO_3^-]$ are "high enough" and $[H_2O_2]$ is "low enough". The quoted words are not made more exact because the critical values of the last three concentrations are interdependent; the value of $[I^-]$ is set by the reaction system (see eq 22 of V).

Skeleton Mechanism and Computer (G. M. Roe and H. A. Liebhfahsky, to end of 1976)

In V, a skeleton mechanism, intended to be amplified as needed, was presented as a model of the reaction system. It contains 15 specific rates¹⁵ that range from some soundly based on experiment, to others, seemingly reasonable though not measurable. This skeleton mechanism follows; for references to the pertinent literature, see V.

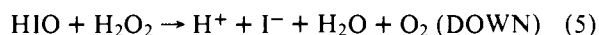
Reversible reactions



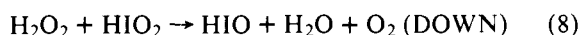
Oxidation of I^+



Reduction of HIO

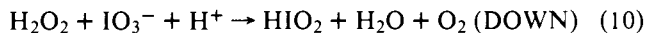


Irreversible reactions forming HIO





Additional formation of HIO_2



The plausibility of this skeleton mechanism was tested on a Honeywell 6000 computer. In this test, which consisted of individual trials by the hundreds, soundly established specific rates were retained, but specific rates less certainly based were changed in value to promote agreement with the experimental data described by eq D. Computations were done for all points in Figures 1, 2, 4, and 5, and for all the "5-s" experiments. Tables I and II contain representative results obtained by feeding into the computer the specific rates listed below.¹⁶ Pertinent comments follow.

1. The computer shows the datum 7.2 min^{-1} to be reconcilable with experimental observations made in this and other reaction systems. It thus strengthens the case for reaction 4 as the only significant UP reaction in this system.

2. The computer fails to reproduce experimental values for F , the second term of eq D. The skeleton mechanism is faulty as regards DOWN and (perhaps) as regards IODINE reactions.

3. On occasion, the computer gave oscillations, but these were unsatisfactory, and found for unrealistic conditions.

4. Owing to the last two points just made, it would be a waste of space to defend the specific rates used. Two points are significant. (1) The value of k_{1r} , palpably exceeds the diffusion limit; it has formal significance only. Its use here is justified for simplicity's sake and because reaction 1 is near equilibrium.¹⁷ (2) If reaction 4 is the only UP reaction, then the stoichiometry of reaction A requires that k_{2f} be 5 times 7.2 min^{-1} ; a total of 10 electrons must be removed from an I_2 molecule, and reaction 4 once through removes only a pair of electrons from I^+ . The specific rate $k_{2f} = 22$ corresponds more nearly to oxidation of I_2 to 2HIO_2 . It has been clear since 1928 that reliable stoichiometric data for this system cannot be obtained. The value of k_{2f} may have to be raised in the future.

5. The computer is only partially successful in dealing with $[\text{I}^-]$, the most nearly controlling among the concentrations. The computer has been signally successful in showing how the skeleton mechanism can accomplish I^- removal, left as a serious problem in V. This problem is solved in a simple way that may be unique to this reaction system.¹⁸

6. According to the computer, the skeleton mechanism gives $[\text{I}^-]$ values correct in order of magnitude (10^{-7} M and less). It does not give $[\text{I}^-]$ values that increase as $[\text{I}_2]$ decreases, a condition found in most experiments; see V, Figure 1, pulse 0 in W-24 or W-27. It does yield the kind of $[\text{I}^-]$ behavior observed in W-100: namely, continuous decrease of $[\text{I}^-]$ so long as I_2 disappears at low $[\text{H}_2\text{O}_2]$.

7. The complexity of the reaction system and the uncertainty of some specific rates combine to underline the importance of searching for the closest possible numerical agreement between measured and computed values of all experimentally accessible quantities.

Acknowledgment. For help of different kinds, we thank the Robert A. Welch Foundation, the School of Aerospace Medicine, and the General Electric Company.

References and Notes

- (1) Part I: W. C. Bray and H. A. Liebhafsky, *J. Am. Chem. Soc.*, **53**, 38 (1931).
- (2) Part II: W. C. Bray and A. L. Caulkins, *J. Am. Chem. Soc.*, **53**, 44 (1931).
- (3) Part III: H. A. Liebhafsky, *J. Am. Chem. Soc.*, **53**, 896 (1931).
- (4) Part IV: H. A. Liebhafsky, *J. Am. Chem. Soc.*, **53**, 2074 (1931).
- (5) Part V: H. A. Liebhafsky and L. S. Wu, *J. Am. Chem. Soc.*, **96**, 7180 (1974).
- (6) Roman numerals will be used to cite the five references just given.
- (7) A. Skrabal, *Z. Elektrochem.*, **40**, 232 (1934).
- (8) H. A. Liebhafsky, *Z. Phys. Chem., Abt. A*, **155**, 289 (1931).
- (9) M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **84**, 1355 (1962).
- (10) (a) R. P. Bell and E. Gelles, *J. Chem. Soc.* 2734 (1951); (b) J. D. Burger and H. A. Liebhafsky, *Anal. Chem.*, **45**, 600 (1973).
- (11) I. Matsuzaki, R. Simic, and H. A. Liebhafsky, *Bull. Chem. Soc. Jpn.*, **45**, 3367 (1972).
- (12) Conventions are those of V: time, minutes or seconds, as indicated; concentrations, moles/L, represented by []; stoichiometric equations, =; kinetic processes, \rightarrow for irreversible, and \rightleftharpoons for reversible reactions; rates, R 's, and specific rates, k 's, are identified by subscripts.
- (13) The apparent increase in $[\text{I}_2]$ upon the first H_2O_2 addition in W-100 is a red herring often observed upon such occasions, when O_2 bubbles are suddenly formed in a stirred reaction mixture. Owing to internal reflection and scattering of the spectrophotometric light beam, such bubbles reduce apparent transmittance. The bubbles are evidence of a rapid DOWN reaction, probably that of HIO with H_2O_2 .
Oxygen supersaturation is a vexing problem in all rate measurements of oxygen evolution. There is no evidence that the formation of oxygen bubbles, which must have been greatly different in the conventional and the stopped-flow equipment, measurably affected the rate of iodine disappearance.
- (14) The skeleton mechanism (next section) contains two UP reactions: 4 and 9. Under our conditions, R_9 is negligible in comparison with $7.2[\text{I}_2]$.
- (15) The number of specific rates grows to 15 because two reactions (9 and 10) have rate laws in which one term is independent of—and the second proportional to— $[\text{H}^+]$: the two latter are listed as k_9' and k_{10}' .
- (16)

k_{1f}	k_{1r}	k_{2f}	k_{2r}	k_{3f}	k_{3r}	k_4	k_5	k_6
2130	51.7E13	22	12E9	30E4	1E6	1.37E7	6.5E3	2E11
k_7	k_8	k_9	k_9'	k_{10}	k_{10}'			
1E9	1	4.18	38.9	2.6E-4	129E-4			

All values for 50°C . Unit time, the minute. Concentrations, moles/L. "E" means "exponent of 10"; thus, 1E4 is $1(10^4)$ and 1E-4 is $1(10^{-4})$. See references listed in V for background information on the skeleton mechanism.
- (17) The possibility remains that a more detailed mechanism for reaction 1 will be needed to explain the oscillatory reaction; see ref 9.
- (18) The computer makes I_2 "go one way" (reaction 2f) and "return another" (reaction 1r), creating a "GOWRA" mechanism by the head-and-tail coupling (through I_2 and I^-) of two reversible reactions with specific rates suitably related. Computer data for W-27 at 5 s are illustrative:

$$-R_{1f} - (-R_{1r}) = -R_{1(\text{NET})} \qquad -R_{2f} - (-R_{2r}) = -R_{2(\text{NET})}$$

$$+1.775 - 1.788 = -0.013 \qquad +0.01833 - 0.00001 = +0.01832$$

(rates in moles of $\text{I}_2 \text{ L}^{-1} \text{ min}^{-1}$). Positive numbers, I_2 is disappearing; negative, I_2 is forming. Computer value of $[\text{I}_2]$, 0.00083.)
This is a remarkable situation. Reaction 1r is returning I_2 at 71% the rate I_2 is disappearing via reaction 2f. To do this, reaction 1 need be displaced from equilibrium by only 0.7%, a displacement that would be considered negligible in most reaction systems, in which complete equilibrium would consequently be assumed. Note particularly that neither complete equilibrium, nor microscopic reversibility, nor a Bodenstein steady state was assumed here.
The "GOWRA" principle seems correct but the mechanism of reaction 2f may need further modification; see comment 4 above.