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Francis James Hughes
Iowa State College

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THE KINETICS OF THE HYDROGEN PEROXIDE OXIDATION OF SELENIOUS ACID

by

Francis J. Hughes

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

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I. INTRODUCTION

Four frequently used methods of preparation of selenic acid from selenious acid have been described. These include the action of bromine on silver selenite,[1] the oxidation of selenious acid by chloric acid,[2] the electrolysis of selenious acid[3] and the oxidation of selenious acid by hydrogen peroxide.[4] This last method has been the most convenient on a laboratory scale and has yielded an exceedingly pure product since the excess of reagent can be removed completely by a vacuum distillation. The complete reaction is accomplished only by refluxing for an extended period of time (24 hours or more) with occasional addition of more hydrogen peroxide.

Under conditions in which the reaction proceeds at a satisfactory rate, the evolution of gas which is always observed indicates a considerable decomposition of hydrogen peroxide to oxygen and water.

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

The rate of the above reaction is greater than that of the actual oxidation of the Selenious acid as represented in the reaction

$$H_2O_2 + H_2SeO_3 \longrightarrow H_2O + H_2SeO_4$$

Consequently a large excess of hydrogen peroxide must always be employed.

In some preparations which were carried out under conditions that were believed effective for complete conversion of selenious acid to selenic acid, positive tests for selenite were still obtained by the sulfurous acid method.[4] These results indicated possible decomposition of selenic acid, its reduction by hydrogen peroxide, or perhaps some unusual feature of the kinetics of the oxidation.

The work described in this thesis was undertaken to investigate in detail the kinetics of this oxidation-reduction reaction in order that optimum synthetic procedures could be formulated and that information could be provided concerning the mechanism of the process.

The overall equation for this reaction corresponds to a transfer of an oxygen atom from a hydrogen peroxide molecule to a selenious acid species. From the energetics of possible transition states it appears unlikely that the transfer is effected in a single bimolecular collision process.

Selenic acid oxidations are in general quite slow. Equilibrium of the selenite-selenate couple with the chlorine-chloride couple was established in four to seven days at 25°C.[5] With the bromine-bromide couple it was not attained until fifty to seventy days after initial contact.[5] The oxidation potential of the selenite-selenate couple has been given as - 1.15 volts[6] on the basis of the work of

Sherrill and Izard.[5] Well known analytical procedures depend on the fact that selenic acid is not reduced by sulfurous acid at an appreciable rate while selenious acid, a weaker oxidizing agent, is rapidly reduced.[7] ($Se + 3H_2O \longrightarrow H_2SeO_3 + 4H^+ \ 4e$; $E^\circ = -0.74$ volts)[6] In addition, selenic acid is not affected by hydrogen sulfide or ferrous ion despite the high oxidation potential.[6]

Mechanisms for homogeneously catalyzed hydrogen peroxide decompositions have fallen into two groups. One group has included the formation and action of free radicals whereas the other group has involved molecular and ionic species only.

Haber and Weiss[8] proposed a free radical chain mechanism involving OH and HO_2 radicals as intermediates in an attempt to explain the catalytic decomposition of hydrogen peroxide by ferrous and ferric ions.

$$\begin{array}{lll}
Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + OH & & \text{chain initiating} \\
\left.\begin{array}{l} OH + H_2O_2 \longrightarrow HO_2 + H_2O \\ HO_2 + H_2O_2 \longrightarrow O_2 + H_2O + OH \end{array}\right\} & & \text{chain carrying} \\
Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^- & & \text{chain terminating} \\
Fe^{+2} + HO_2 \rightleftharpoons Fe^{+3} + HO_2^- & & \text{chain carrying} \\
Fe^{+3} + HO_2 \longrightarrow Fe^{+2} + O_2 + H^+ & & \text{chain terminating}
\end{array}$$

A significant proposal of the authors was that hydrogen peroxide is never simultaneously attacked by two one-electron reagents nor by a two-electron reagent in either oxidation or reduction. Instead there are one-electron changes involving the formation of either hydroxyl or HO_2 radicals.

The foregoing mechanism has since been modified in some ways. Weiss[9] himself proposed a dissociation of the HO_2 radical in order to account for the acid dependence of the reaction. Evans, Hush, and Uri[10] suggested a comparatively high value for the dissociation constant to allow the more desirable and less complicated reaction

$$O_2^- + H_2O_2 \longrightarrow O_2 + OH^- + OH$$

to replace

$$HO_2 + H_2O_2 \longrightarrow O_2 + H_2O + OH$$

Barb, Baxendale, George, and Hargrave[11] have studied the reaction quite extensively and have pointed out that the most likely main oxygen evolution step is

$$Fe^{+3} + O_2^- \longrightarrow Fe^{+2} + O_2$$

Christiansen and Andersen[12] have stoutly contested the Haber and Weiss mechanism for the iron(II) and iron(III) catalysis of the decomposition of hydrogen peroxide and have proposed

$$Fe^{+3} + HO_2^- \rightleftharpoons FeOOH^{+2}$$

$$FeOOH^{+2} \rightleftharpoons Fe^{+3} + HO_2^{-*}$$

$$HO_2^{-*} + H_2O_2 \longrightarrow O_2 + H_2O + OH^-$$

on the basis of a deviation from a first order dependence on hydrogen peroxide concentration found by Andersen[13] at low hydrogen peroxide concentrations. Uri,[14] on the other hand, has explained the data of Andersen[15] in terms of the modified Haber and Weiss free radical chain mechanism. Peterson[16] has failed to obtain Andersen's rate law when the nitrate in the system is completely replaced by perchlorate.

Cahill and Taube[17] have postulated the system

$$\left.\begin{array}{llllll} Fe^{+3} & + \; H_2O_2 & \rightleftharpoons & FeOOH^{+2} & + \; H^+ & \\ FeOOH^{+2} & & \longrightarrow & Fe^{+2} & + \; HO_2 & \\ Fe^{+3} & + \; HO_2 & \longrightarrow & Fe^{+2} & + \; O_2 & + \; H^+ \end{array}\right\}\text{chain initiating}$$

$$\left.\begin{array}{llllll} Fe^{+2} & + \; H_2O_2 & \longrightarrow & Fe^{IV} & + \; 2OH^- & \\ Fe^{IV} & + \; H_2O_2 & \longrightarrow & FeOOH^{+3} & + \; H^+ & \\ FeOOH^{+3} & & \longrightarrow & Fe^{+3} & + \; HO_2 & \\ Fe^{+3} & + \; HO_2 & \longrightarrow & Fe^{+2} & + \; H^+ & + \; O_2 \end{array}\right\}\text{chain carrying}$$

$$\left.\begin{array}{llllll} Fe^{+2} & + \; H_2O_2 & \longrightarrow & Fe^{+3} & + \; OH^- & + \; OH \\ Fe^{+2} & + \; OH & \longrightarrow & Fe^{+3} & + \; OH^- & \end{array}\right\}\text{chain terminating}$$

There were two main features to be explained by this mechanism. The isotope fractionation factor of O^{18} appearing in the water was the same in the reaction of hydrogen peroxide with iron(II) as it was in the reaction of hydrogen peroxide with several reagents which underwent two-electron changes, and different from that obtained from titanium(III), a one-electron reducing agent. In addition, iron(III) led to an isotope fractionation factor similar to that of iron(II). From these considerations the authors decided that any mechanism for the iron reaction with hydrogen peroxide had to incorporate iron(II) as a reaction intermediate and iron(IV) as the result of a two-electron loss by iron(II).

The reaction of nitrous acid with hydrogen peroxide has been studied by two groups of investigators with differing results.[18,19] It is of interest that the proposed reaction intermediate, peroxynitrous acid, can be observed.

Shilov and Stepanova[18] found the rate law to be

$$\frac{d(H_2O_2)}{dt} = k(H_2O_2)(HNO_2)^2 + k'(H_2O_2)(HNO_2)(H^+)$$

where ( ) represents concentration.

They proposed the mechanism

$$H_2O_2 + HNO_2 \rightleftharpoons HOONO + H_2O$$

$$HOONO + HNO_2 \longrightarrow HNO_2 + HNO_3$$

$$HOONO + H^+ \longrightarrow H^+ + HNO_3$$

Halfpenny and Robinson[19] reported no term second order in nitrous acid. Instead, their rate law was simply

$$\frac{d(H_2O_2)}{dt} = k(H_2O_2)(HNO_2)(H^+)$$

and their proposed mechanism was

$$NO_2^- + H^+ \longrightarrow HNO_2$$

$$\begin{array}{lllll} HNO_2 + H_2O_2 & \longrightarrow & HOONO + H_2O & & \text{rate determining at low acidity} \\ HOONO & \longrightarrow & OH + NO_2 & & \\ HO + NO_2 & \longrightarrow & HNO_3 & & \end{array}$$

For solutions high in hydrogen peroxide concentration they included the familiar chain of Haber and Weiss.

$$\begin{array}{lll} HO + H_2O_2 & \longrightarrow & H_2O + HO_2 \\ H_2O_2 + HO_2 & \longrightarrow & HO + H_2O + O_2 \end{array}$$

It is evident that some explanation is necessary for the disagreement of rate expressions obtained by the two groups of investigators. Since the work of Shilov and Stepanova was seen only in abstract it is difficult to comment on it. On the other hand, Halfpenny and Robinson[19] have covered only a limited range of nitrous acid concentrations (0.00125 - .00171M), have obtained their rate expression from extrapolated initial slopes, and have not mentioned adjustment of the ionic strengths of their solutions.

The Haber and Weiss mechanism has also been used to explain the decomposition of hydrogen peroxide at metal surfaces such as platinum, gold, palladium, silver, and zinc.[20]

$$\left.\begin{array}{lll} H_2O_2 + e(\text{Metal}) & \longrightarrow & OH + OH^- \\ HO_2^- & \longrightarrow & HO_2 + e(\text{to Metal}) \end{array}\right\} \text{chain initiating}$$

$$\left.\begin{array}{lllll} OH & + & e(\text{Metal}) & \longrightarrow & OH^- \\ HO_2 & + & e(\text{Metal}) & \longrightarrow & HO_2^- \end{array}\right\} \text{chain terminating}$$

$$\left.\begin{array}{lllll} HO_2 & + & H_2O_2 & \longrightarrow & H_2O + O_2 + OH \\ OH & + & H_2O_2 & \longrightarrow & H_2O + HO_2 \end{array}\right\} \text{chain carrying}$$

The decomposition of hydrogen peroxide in aqueous solution has been extensively studied. Early work by Clayton[21] indicated a first order rate law. Important features, however, were contained in a definitive rate study by Rice and Reiff.[22] Using extreme precautions to ensure pure, dust-free hydrogen peroxide in a reaction vessel with smoothed walls, they observed a slow, almost zero order rate. This rate became first order with induction periods when a small amount of impurity was present.

The Haber and Weiss chain carrying steps have been proposed together with the photochemical step for the photochemical decomposition of hydrogen peroxide in aqueous solution.[23]

$$\begin{array}{l} H_2O_2 + \qquad \longrightarrow 2OH \\ OH + H_2O_2 \longrightarrow HO_2 + H_2O \\ HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH \end{array}$$

Several combinations of the free radicals postulated have been suggested as chain termination steps. Recent work by Hunt and Taube[24] has presented evidence that the chain initiation process is probably

$$H_2O_2 + h\nu \longrightarrow H_2O + O$$

$$O + H_2O_2 \longrightarrow OH + HO_2$$

In contrast to the above group of reactions involving free radical mechanisms is the group of reactions between hydrogen peroxide and a number of anions. Edwards[25] has discussed these reactions in terms of an acid catalysis mechanism common to all of them. They appeared to fit the general rate law

$$\frac{d(H_2O_2)}{dt} = k_1(H_2O_2)(B^x) + k_2(H_2O_2)(B^x)(H^+)$$

where B is the anion in question and x is its charge. The anions included were iodide, bromide, chloride, hypobromite, hypochlorite, iodate, hypoiodite, bromate, thiosulfate, and nitrite. The reaction of hydrogen peroxide with molecular iodine was also included. He proposed that the process was a nucleophilic attack of the reducing agent on the peroxide with a concurrent displacement of a hydroxide ion coupled with a donation of a proton by the general acid to the hydroxide ion being displaced.

In the reaction of hydrogen peroxide with the sulfite ion Halperin and Taube[26] have demonstrated that two atoms of oxygen are transferred from each molecule of peroxide which reacts. Their mechanism for the process involves the formation of peroxysulfurous acid.

$$\mathrm{HO}\overset{O}{\mathrm{S}}\mathrm{OH} + \mathrm{H}\overset{**}{\mathrm{OO}}\mathrm{H} \longrightarrow \mathrm{HO}\overset{O}{\mathrm{S}}\overset{**}{\mathrm{OO}}\mathrm{H} + H_2O$$

The peroxysulfurous acid then rearranges either by itself or by interaction with another sulfite ion.

In the present study it was anticipated that the selenious acid reaction would further elucidate the general subject of anionic hydrogen peroxide decompositions.

II. EXPERIMENTAL

A. Materials

1. Selenium

Selenium was obtained as a 99.95% pure product from the A. D. Mackay Company in the form of small black pellets.

2. Selenious acid

A nitric acid oxidation[27] was used in the preparation of selenious acid. Selenium was dissolved in nitric acid and the solution was boiled to dryness to drive off the excess nitric acid. Water was added and the solution was again boiled to dryness. This last step was repeated twice. Finally, the selenium dioxide was sublimed in a beaker to form long needlelike crystals. These were scraped off the walls of the beaker and dissolved in water to form selenious acid.

3. Hydrogen peroxide

Hydrogen peroxide was obtained in reagent grade, free from inhibitors, and approximately 30% by weight, from the J. T. Baker Chemical Company.

4. Selenic acid

Selenic acid was prepared according to the procedure given by Gilbertson and King.[4] Selenious acid was allowed to stand for twenty-four hours in the presence of 30% hydrogen peroxide. The mixture was then refluxed for twenty-four hours while oxygen was bubbled through the solution. The hydrogen peroxide and most of the water were removed by vacuum distillation.

5. Iron(III) perchlorate

Iron(III) perchlorate was prepared from reagent grade iron(III) nitrate. The latter compound was dissolved in water and treated with a solution of reagent grade sodium hydroxide to precipitate iron(III) hydroxide. The precipitate was collected on filter paper, washed with water, and dissolved in reagent grade perchloric acid. The perchloric acid was then neutralized with reagent grade ammonium hydroxide which reprecipitated the iron(III) hydroxide. This was redissolved in perchloric acid, precipitated with ammonium hydroxide, washed with water, and dissolved in dilute perchloric acid to make a stock solution. The stock solution was standardized by spectrophotometric comparison with several standard solutions prepared from reagent grade iron wire.

6. Lithium perchlorate

Lithium perchlorate was obtained in reagent grade from the G. Frederick Smith Chemical Company. Insoluble particles were eliminated from this compound by the filtration of an aqueous solution.

7. Platinum

The sheet platinum used as a surface catalyst was obtained from the J. Bishop and Company Platinum Works.

8. Radioactive selenium

The selenium^{75} for the exchange experiment was part of a 5 millicurie shipment received from the Oak Ridge National Laboratory. It was originally in the form of selenious acid in a hydrochloric acid solution. It was further purified by precipitation of the selenium with hydrazine hydrochloride and reconversion to selenious acid by the procedure mentioned in Part 2 above.

9. Analytical standards

The primary standards used in standardizing the various solutions were iron wire, potassium acid phthalate, and ethylenediamine iron(II) sulfate. All of these were reagent grade chemicals.

B. Analyses

In most cases the components of the reaction mixtures were selenious acid, selenic acid, perchloric acid, hydrogen peroxide, and water. Usually there was no selenic acid present initially; but in the few reaction mixtures which contained selenic acid initially, there was no perchloric acid. Therefore three analyses were sufficient to determine the system, total acidity, selenious acid, and hydrogen peroxide.

Both the total acidity and the selenious acid were determined by a potentiometric titration with standardized sodium hydroxide. The difference between the first and the second end-points was proportional to equivalents of selenious acid in the solution. Some difficulty was experienced in obtaining exact values for the concentrations of selenious acid. It was found that the presence of carbonate in the sodium hydroxide solution was the source of error. The error was kept to within 2.0% by careful preparation and storage of the sodium hydroxide solution. The solution was prepared by filtering a saturated aqueous solution of sodium hydroxide into hot, boiled, distilled water. This solution was kept in a large bottle with an ascarite-magnesium perchlorate trap to exclude carbon dioxide from the air entering the bottle.

The potentiometric determination of the selenious acid was accurate to ± 5% because of the difficulty in reading the second end-point. It was certainly not a rapid method of analysis but was the best of the methods considered. Two other methods contemplated were the determination of selenium which involved selective reduction of selenious acid by sulfurous acid, and the gravimetric determination of barium selenate after precipitation from a nitric acid solution. These methods were not, however, well adapted to small amounts of selenious and selenic acids.

A cerium(IV) titration was employed to determine the hydrogen peroxide in the samples withdrawn from the reaction mixtures. The cerium(IV) solution was 1 M with respect to sulfuric acid, and the yellow color of the cerium(IV) was sufficient to indicate the end-point. Selenious acid does not interfere with this determination.[28]

In the exchange experiment it was necessary to separate selenious acid from selenic acid. This was done by slowly adding sulfurous acid to each sample. When the peroxide was consumed, the selenious acid was reduced to selenium which was filtered, washed, dried, and mounted for counting.

Small amounts of iron(III) were determined by conversion to the salicylate with subsequent spectrophotometric comparison with standard iron(III) salicylate solutions.[29]

C. Apparatus

All the reactions were carried out in a Precision Scientific Company water bath in which the temperature was held constant to ± 0.1°C.

Both pyrex glass stoppered flasks and polyethylene containers were used to contain the reaction mixtures.

These reaction vessels were closed to the air but were not sealed against evolution of gas by the reaction mixture. The containers were cleaned initially by several hours of steaming but were merely rinsed thoroughly with double distilled water between experiments. The pyrex glass helices which were used to increase the available surface area in some of the reaction were also cleaned by steaming.

Potentiometric titrations were performed with a Beckman Model G pH meter together with a Type E high pH glass electrode as the indicator electrode and a saturated calomel electrode as the reference electrode.

A Tracerlab Geiger-Mueller counter was used in conjunction with a Nuclear Instrument and Chemical Corporation Model 165 scaling unit for the counting of radioactive samples.

Analyses of solutions for small quantities of iron were carried out with a Beckman Model D.U. Spectrophotometer.

D. Procedure

Each reaction mixture was prepared by the pipetting into the reaction vessel of the proper quantities of stock solutions of all the reagents required to produce the initial concentrations of materials with the exception of hydrogen peroxide. The mixture was brought to temperature in the water bath, and the necessary amount of hydrogen peroxide was added. The flask was shaken several times below the surface of the water to ensure complete mixing. In every case the initial ionic strength was 1.7 M. Mixtures of low acidity were adjusted to an ionic strength of 1.7 M by the addition of the calculated amount of lithium perchlorate.

Samples of two milliliters each were pipetted from the reaction mixtures at various intervals during the course of the reaction. The pipette was rinsed with the reaction mixture before each sampling. Two samples were taken at a time, and the reactions were quenched by cooling to room temperature. One of the samples was titrated for the hydrogen peroxide content while the other one was titrated potentiometrically for both selenious acid content and total acidity.

In the treatment of the radioactive samples the sulfurous acid method was used to separate selenious acid from selenic acid. The selenium obtained from the reduction of the selenious acid was dried, counted, and weighed in order to determine its specific activity.

III. RESULTS

A. Conversion of Analytical Results to Rate Data

Since the rates of reaction of both selenious acid and hydrogen peroxide depended upon many variables, a simple plot of the data did not suffice to resolve the system. It was found necessary to plot the concentrations of the reactants versus time and to measure the slopes of the curves at various intervals. These slopes were tabulated together with the concentrations of the reactants at the respective times. Table 1 contains several arbitrary selections of groups of data from each reaction.

At the temperatures of the reaction mixtures evaporation had to be considered. Since the total replaceable hydrogen in the solution did not change as a result of the reaction, the increase of total acidity of the solution with time was a measure of the amount of evaporation of the solution. This was not of great enough magnitude to be important in most of the reactions, but in the case of reactions carried out in polyethylene containers, a correction term was found to be necessary. If V = volume of solution in liters, A = total replaceable hydrogen in moles, c_a = concentration of total replaceable hydrogen in moles per liter, M = moles of reactant in solution, and

Table 1

Data from Reactions

Reaction Number	Time (hours)	(H_2SeO_3) m/l	(H_2O_2) m/l	$(HClO_4)$ m/l	(H_2SeO_4) m/l	(H^+) m/l	$\frac{d\,(H_2SeO_3)}{dt}$ m/l-hr.	$\frac{d(H_2O_2)}{dt} - \frac{d\,(H_2SeO_3)}{dt}$ m/l-hr.
6	0	0.548	0.499	1.640	0	1.640	0.00254	0.00154
6	30	0.487	0.399	1.640	0.061	1.701	0.00154	0.00121
6	60	0.451	0.329	1.640	0.097	1.737	0.00098	0.00093
7	0	0.487	2.47	1.233	0	1.233	0.01197	0.0227
7	20	0.334	2.00	1.233	0.153	1.386	0.00448	0.0142
7	40	0.277	1.70	1.233	0.210	1.443	0.00197	0.0101
9	0	0.503	0.099	1.717	0	1.717	0.00048	0
11	0	0.493	2.46	0.992	0	0.992	0.01420	0.0243
11	30	0.289	1.78	0.992	0.204	1.196	0.00345	0.0114
11	70	0.209	1.37	0.992	0.284	1.276	0.00131	0.0061
12	0	0.482	2.47	1.772	0	1.772	0.00890	0.0203
12	30	0.330	1.87	1.772	0.152	1.924	0.00304	0.0108
12	80	0.230	1.39	1.772	0.252	0.024	0.00117	0.0057
15	0	0.486	2.50	0	1.717	1.717	0.01033	0.0511
15	20	0.301	1.71	0	1.842	1.842	0.00393	0.0156
15	50	0.284	1.17	0	1.919	1.919	0.00182	0.0110
18	0	0.533	1.62	1.968	0	1.968	0.00640	0.0128
18	30	0.404	1.20	1.968	0.129	2.097	0.00313	0.0075
18	60	0.338	.97	1.968	0.195	2.163	0.00151	0.0049
19	0	0.485	2.47	0.253	0	0.253	0.0542	0.0422
19	15	0.249	1.87	0.253	0.236	0.489	0.00615	0.0161
19	30	0.191	1.62	0.253	0.294	0.547	0.00279	0.0106
19	60	0.137	1.32	0.253	0.348	0.601	0.00100	0.0065

Table 1 - Continued

Reaction Number	Time	(H_2SeO_3)	(H_2O_2)	$(HClO_4)$	(H_2SeO_4)	(H^+)	$\frac{d\,(H_2SeO_3)}{dt}$	$\frac{d(H_2O_2)}{dt} - \frac{d\,(H_2SeO_3)}{dt}$
20	0	0.486	2.48	0.501	0	0.501	0.0275	0.0294
20	15	0.298	1.95	0.501	0.188	0.689	0.00619	0.0169
20	50	0.190	1.45	0.501	0.296	0.797	0.00163	0.0080
21	0	0.550	1.005	1.727	0	1.727	0.00461	0.00551
21	30	0.455	0.776	1.727	0.095	1.822	0.00194	0.00354
21	60	0.411	0.642	1.727	0.139	1.866	0.00119	0.00241

c_m = concentration of reactant im moles per liter, the rate of change per unit volume of the total reactant due to the reaction is

$$\frac{1}{V}\frac{dM}{dt} = \frac{dc_m}{dt} + c_m \frac{d\, Ln\, V}{dt}$$

The last term may be evaluated from the expression

$$\frac{d\, Ln\, V}{dt} = - \frac{d\, Ln\, c_a}{dt}$$

The data for the reactions carried out in polyethylene containers include the proper evaporation correction terms.

B. Determination of Rate Laws

1. The selenious acid reaction

Variation of selenious acid concentration with time for a typical reaction, #12, is shown in Figure 1. Although many of the reactions were followed for as long as 400 hours, it can be seen from the graph that the slope of the curve at 100 hours is but a small fraction of the initial slope.

In several experiments the initial selenious acid concentration was approximately 0.5 M, the initial hydrogen ion concentration was approximately 1.7 M, and the initial hydrogen peroxide concentration varied between 0.5 M and 2.0 M. When the initial rates of these reactions were

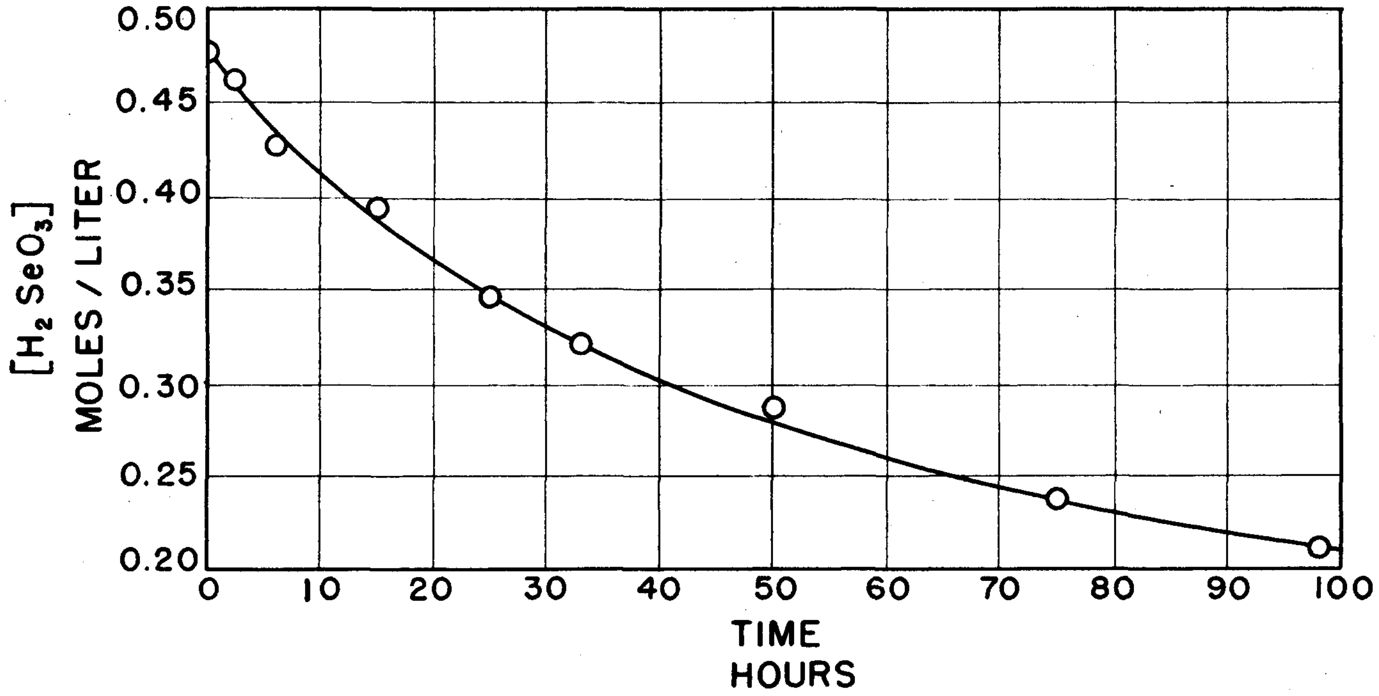


Figure 1. Selenious Acid Concentration Versus Time for a Typical Reaction.

Initial Concentrations: $(H_2O_2) = 2.47$ M

$(HClO_4) = 1.772$ M.

plotted against the hydrogen peroxide concentration, a straight line relationship was obtained as illustrated in Figure 2. The highest point does not conform to the linearity because the initial hydrogen ion concentration in that case was approximately 1.9 M.

When the initial value of the function, $[1/(H_2O_2)]$ $[d(H_2SeO_3)/dt]$, for a group of reactions whose initial hydrogen ion concentration was approximately 1.7 M was plotted versus the square of the concentration of selenious acid, a straight line function was obtained which passed through the origin. The relationship is shown in Figure 3.

In order to establish the hydrogen ion dependence, experiments were conducted in which the initial concentrations of reactants were the same with the exception of the hydrogen ion concentrations. In each case the initial ionic strength was 1.7 M. When the function $[1/(H_2O_2)(H_2SeO_3)^2]$ $[d(H_2SeO_3)/dt]$ was plotted against the reciprocal of the hydrogen ion concentration as in Figure 4, a straight line was obtained which passed through the origin. The rate law therefore took the form

$$-\frac{d(H_2SeO_3)}{dt} = \frac{k_1(H_2O_2)\ (H_2SeO_3)^2}{(H^+)}$$

where $k_1 = 0.0265 \pm 0.0015$ liters /moles -hour at 67.7°C.

A test of the rate law is shown in Figure 5. Various instantaneous values of compositions were selected at random

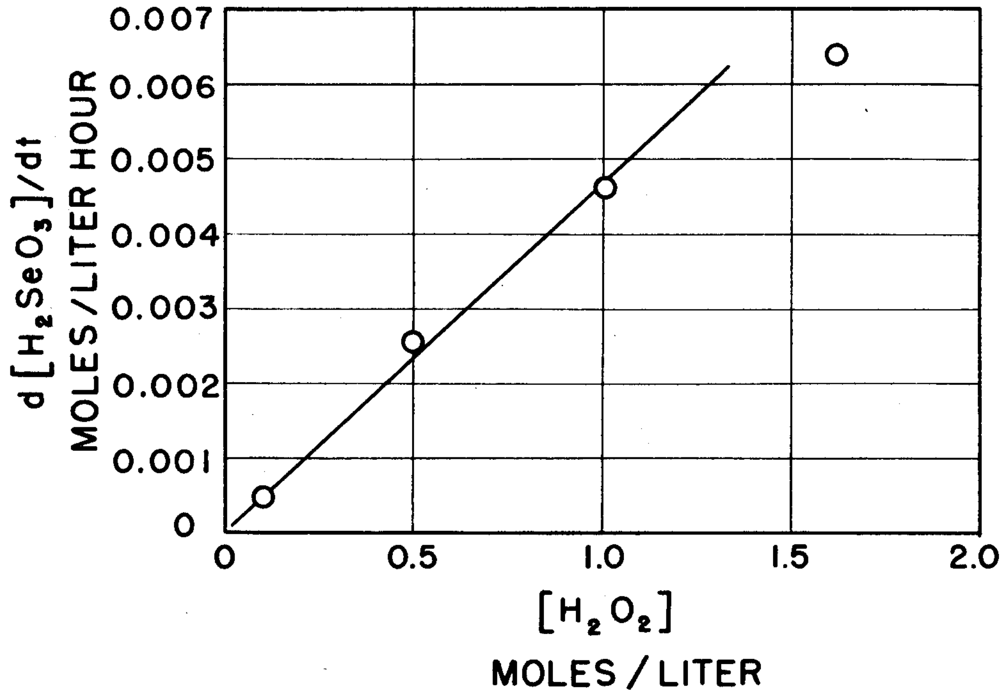


Figure 2. Dependence of Selenious Acid Oxidation Rate upon Hydrogen Peroxide Concentration.

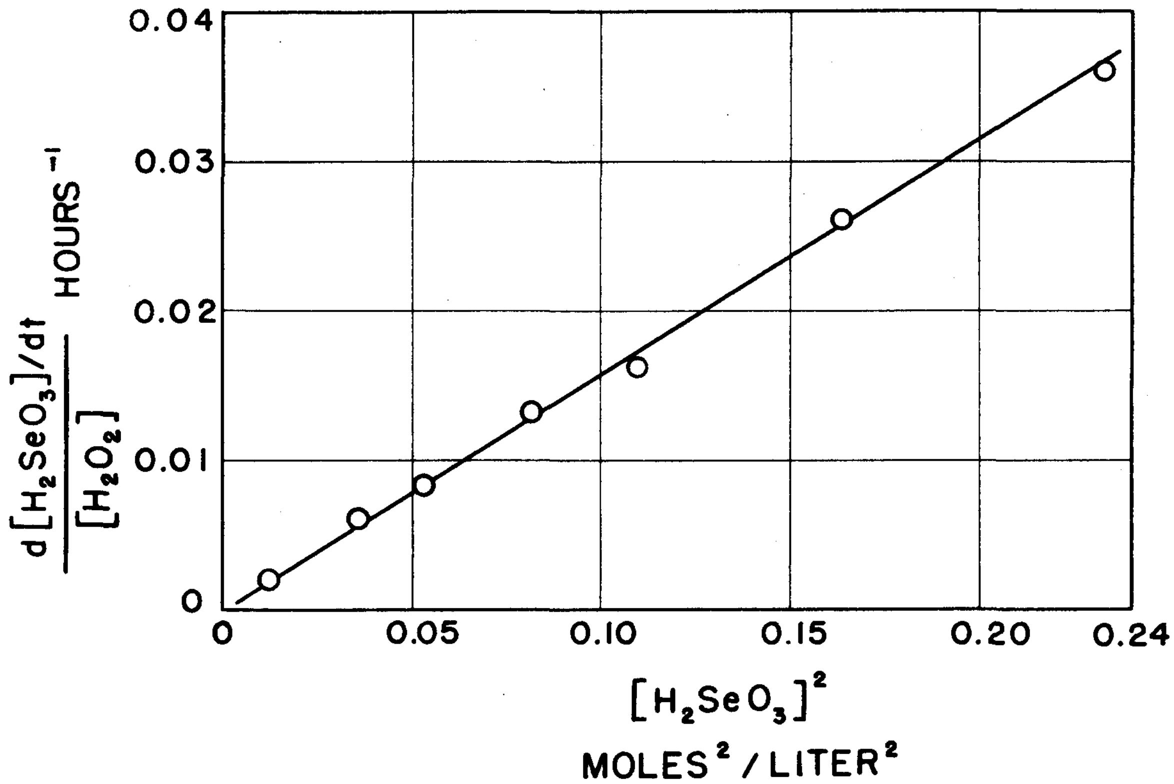


Figure 3. Dependence of Selenious Acid Oxidation Rate upon Selenious Acid Concentration.

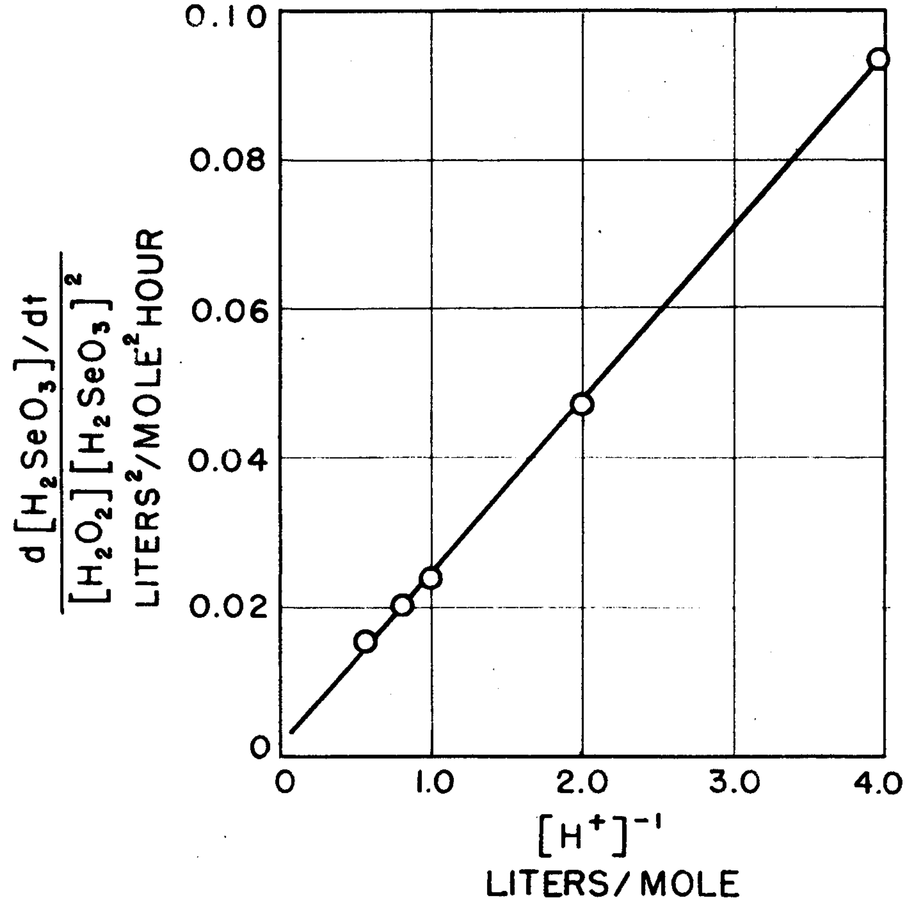


Figure 4. The Dependence of the Selenious Acid Oxidation Rate upon Hydrogen Ion Concentration.

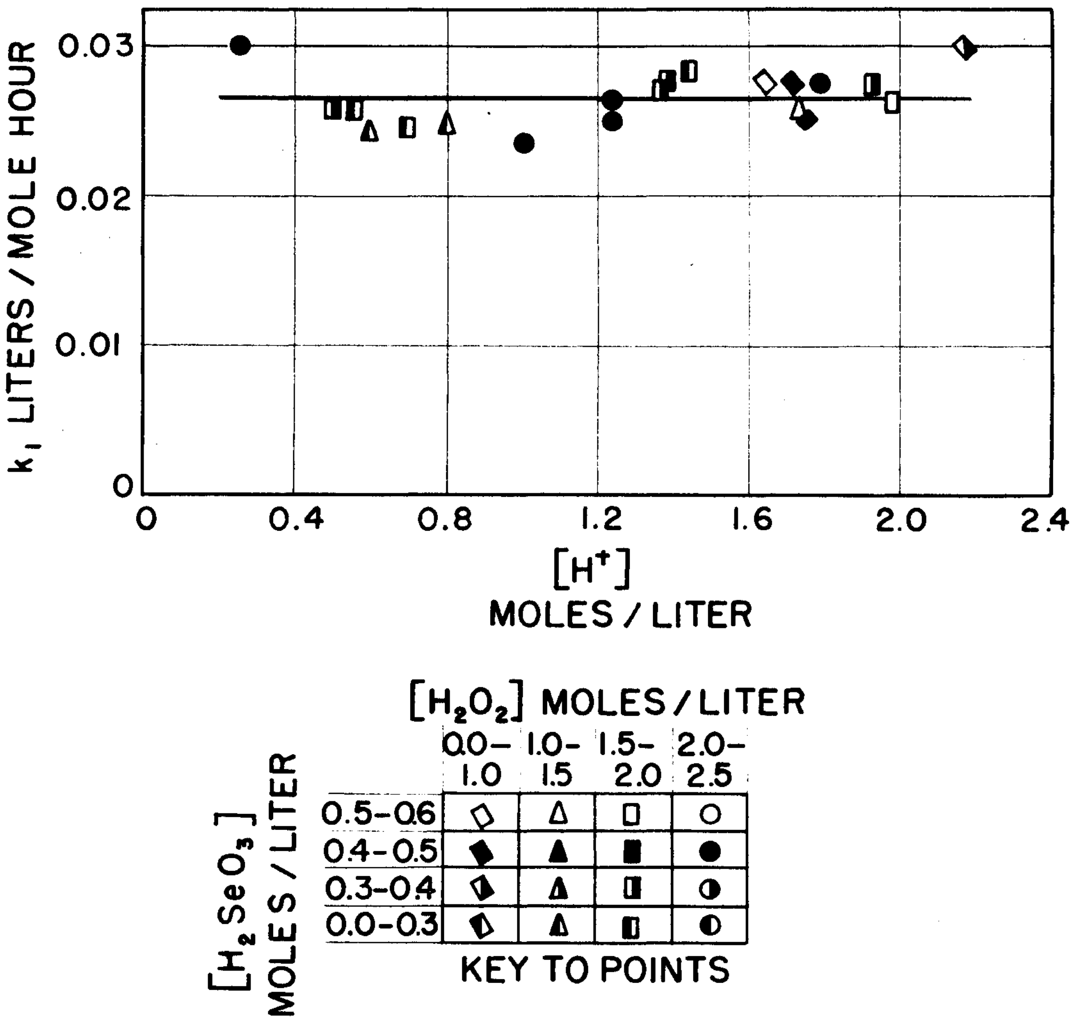


Figure 5. A Test of the Selenious Acid Oxidation Rate Law.

from several different reactions. The rate constant was calculated for each composition by appropriate multiplication and division of the reactant concentrations. These constants were then plotted versus the hydrogen ion concentration. A key explains the ranges in which the other concentrations fall.

Since the rate constant was found to be the same for solutions in which the selenic acid concentration varied widely, it was concluded that the selenious acid oxidation rate did not depend on the concentration of selenic acid.

2. The hydrogen peroxide reaction

Variation of the concentration of hydrogen peroxide with time for a typical reaction is shown in Figure 6. The rate of disappearance of hydrogen peroxide was greater than the rate required to account for the selenious acid oxidation. Evidently the oxidation reaction was accompanied by some decomposition of hydrogen peroxide to form oxygen and water. To find this hydrogen peroxide decomposition rate, the selenious acid oxidation rate was subtracted from the gross hydrogen peroxide disappearance rate. The decomposition rate so obtained was found to be dependent upon the hydrogen peroxide, selenious acid, hydrogen-ion, and selenic acid concentrations.

The results obtained from a group of experiments in which the hydrogen peroxide concentration was varied are

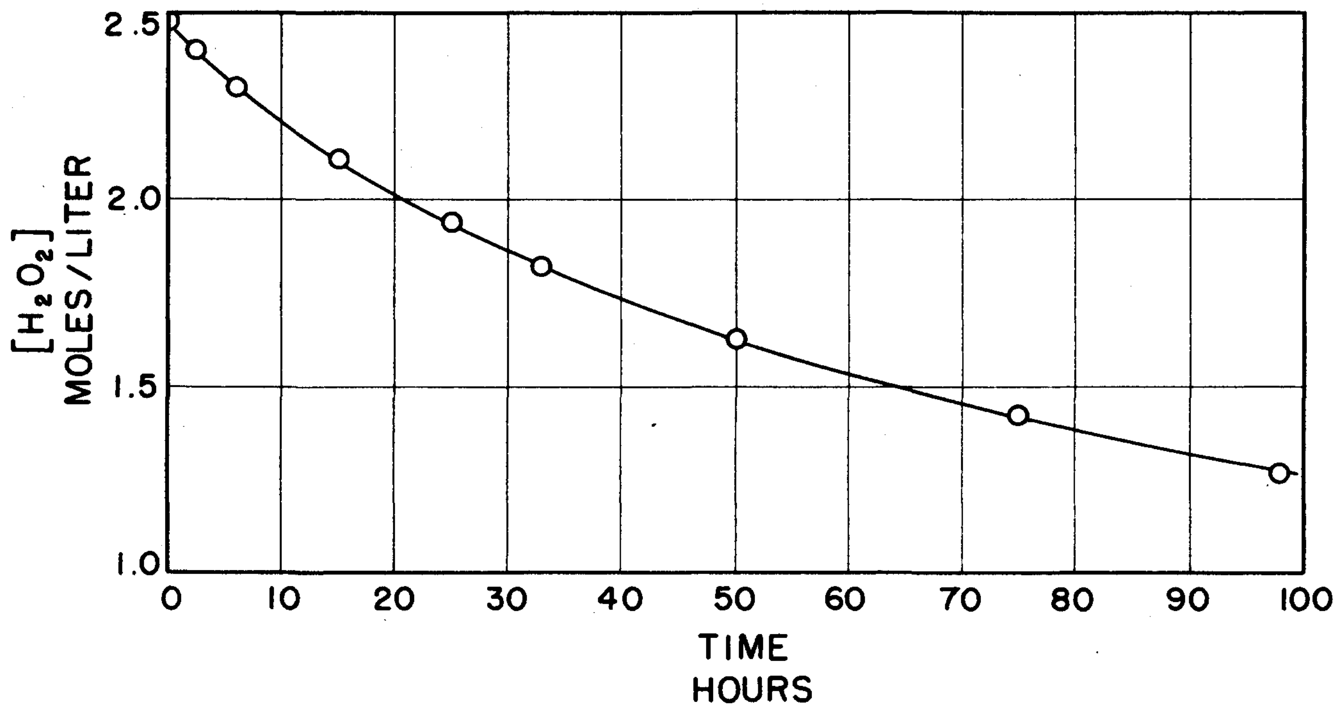


Figure 6. Variation of Hydrogen Peroxide Concentration with Time for a Typical Reaction.

shown in Figure 7 in which the hydrogen peroxide decomposition rate was plotted against hydrogen peroxide concentration. Each point represents the initial rate in an experiment at a time at which no selenic acid was present. The selenious acid concentration for each point was in the neighborhood of 0.5 M while the hydrogen-ion concentration was approximately 1.75 M. Either of the functions below satisfactorily describe the data.

$$-\frac{d(H_2O_2)}{dt} = a(H_2O_2) + b(H_2O_2)^2$$

and

$$-\frac{d(H_2O_2)}{dt} = q(H_2O_2)^{3/2}$$

Curve A represents the contribution of a term first, order in hydrogen peroxide while curve B represents a term, second order in hydrogen peroxide. The sum of the two is curve C. Curve D is obtained from a single term three-halves order in hydrogen peroxide.

Figure 8 demonstrates an inverse dependence of the hydrogen peroxide decomposition rate on the hydrogen-ion concentration. The points represent initial rates when no selenic acid was present, and when the selenious acid concentration was in the neighborhood of 0.5 M and the hydrogen peroxide concentration was approximately 2.45 M. The

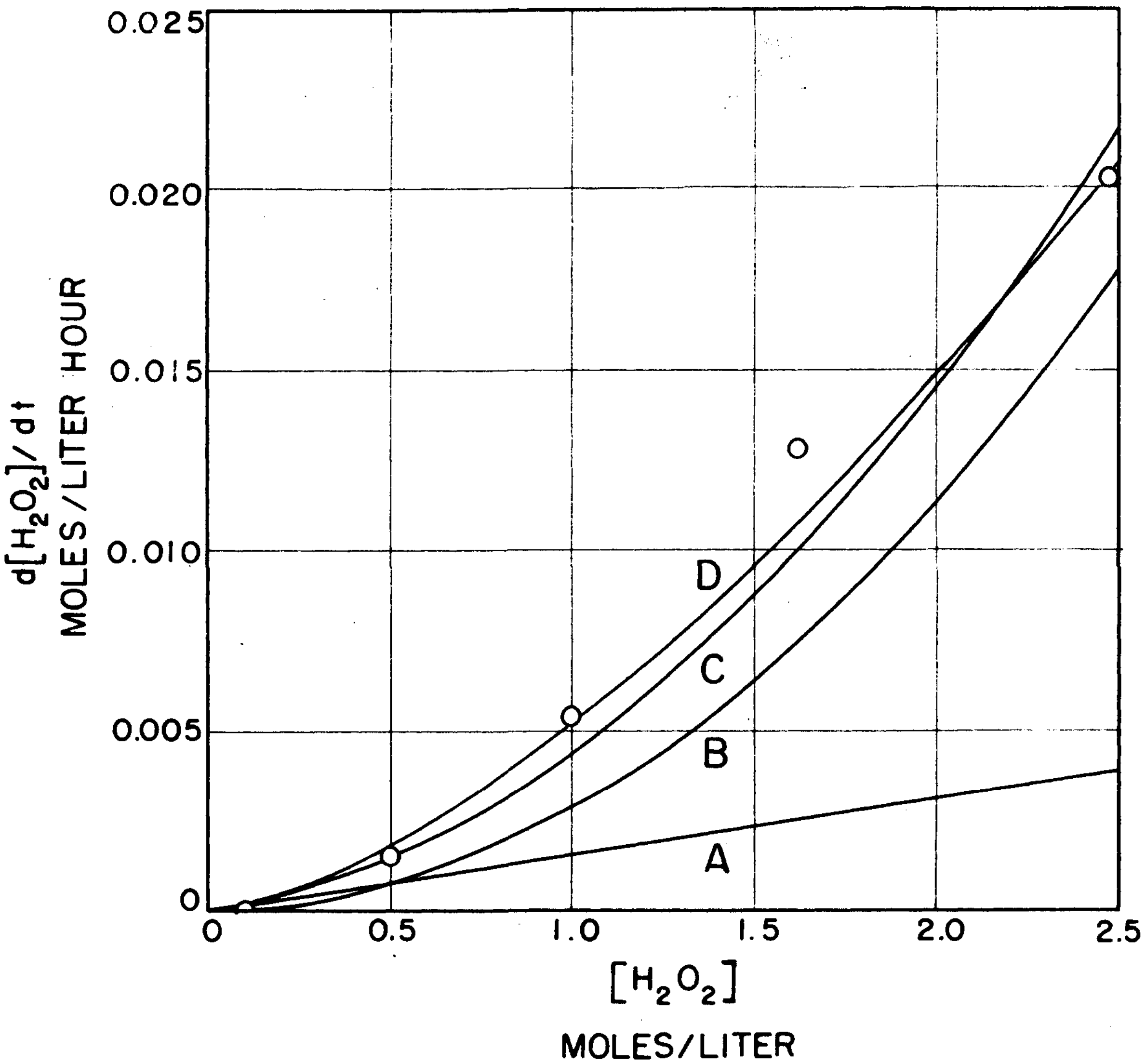


Figure 7. Dependence of Hydrogen Peroxide Disappearance Rate Minus Selenious Acid Oxidation Rate upon Hydrogen Peroxide Concentration.

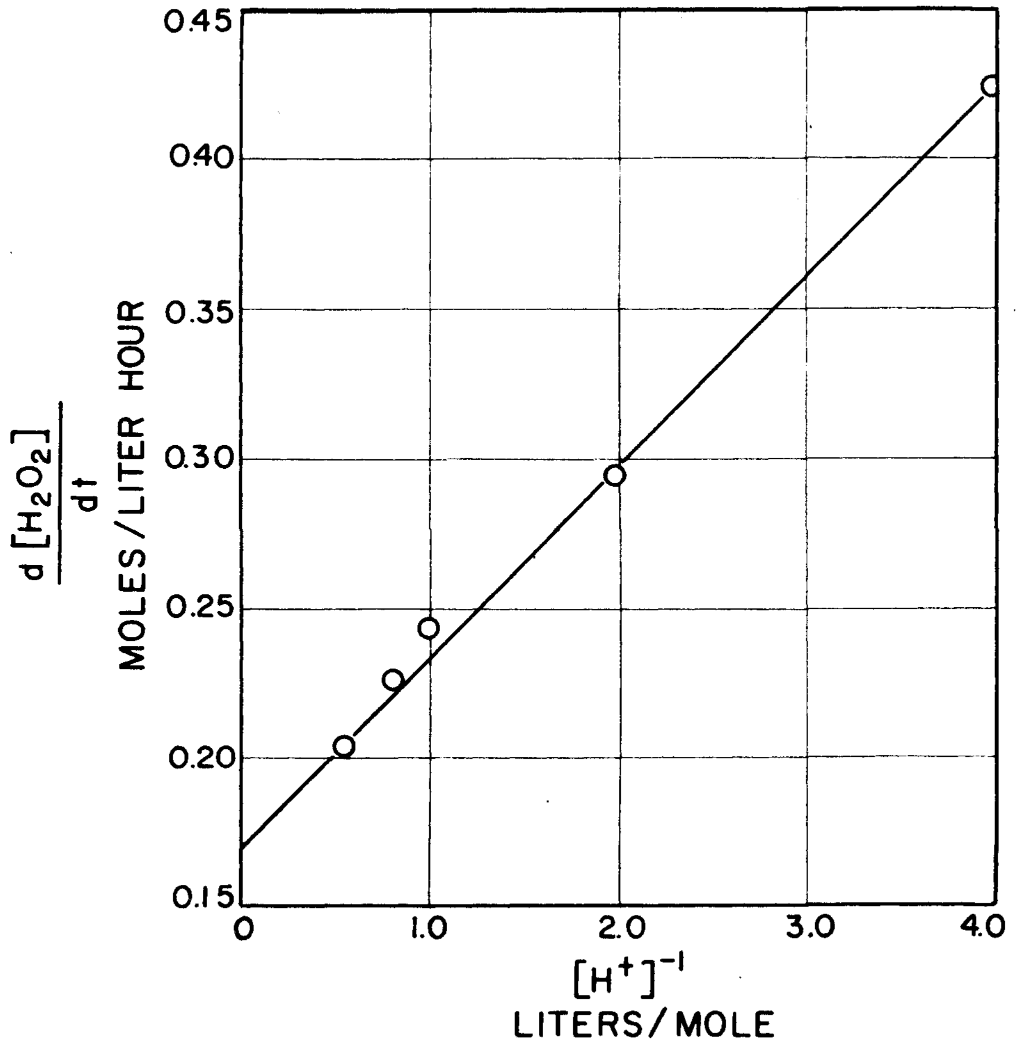


Figure 8. Dependence of Hydrogen Peroxide Decomposition Rate Minus Selenious Acid Oxidation Rate on Hydrogen-Ion Concentration.

straight line relationship of the points indicates a grouping of the rate terms into one expression independent of hydrogen-ion concentration and one expression inversely proportional to hydrogen-ion concentration.

A graph of the hydrogen peroxide decomposition rate versus the selenious acid concentration for constant hydrogen peroxide and hydrogen-ion concentrations is shown in Figure 9. The open circles represent experimental values. At high selenious acid concentrations the rate approaches a first order dependence on the selenious acid concentration. The lower curve is the subtraction of the first order function (middle curve) applying in the upper limit from the total rate (upper curve). This difference may correspond to the surface or dust catalysed decomposition of hydrogen peroxide.

From the data thus far presented, three expressions may be written for the hydrogen peroxide decomposition rate.

$$-\frac{d(H_2O_2)}{dt} = \frac{k_2'(H_2O_2)(H_2SeO_3)}{(H+)} + k_2''(H_2O_2)^2(H_2SeO_3)$$

$$-\frac{d(H_2O_2)}{dt} = \frac{P(H_2O_2)^{3/2}(H_2SeO_3)}{(H^+)} + q(H_2O_2)^{3/2}(H_2SeO_3)$$

and

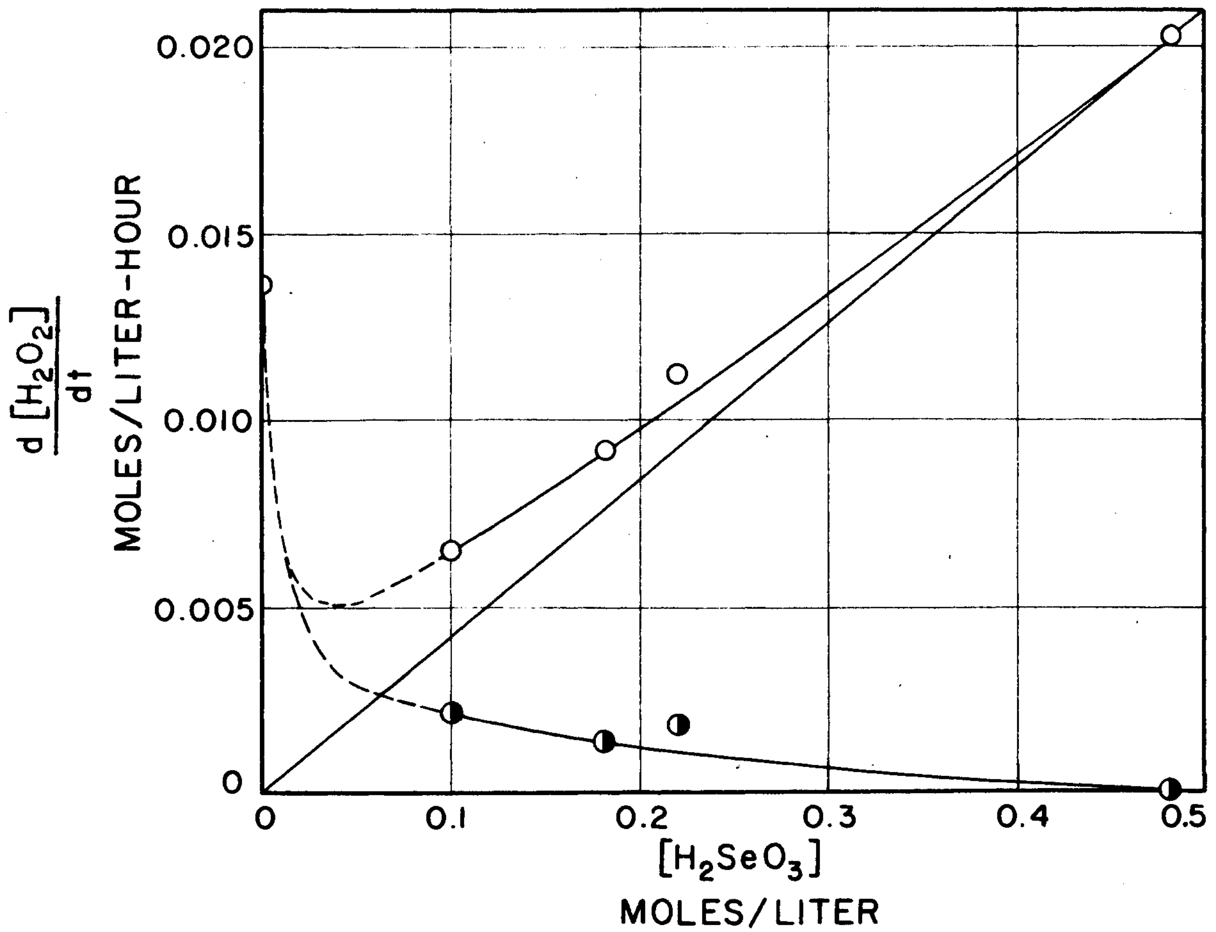


Figure 9. Variation of Hydrogen Peroxide Decomposition Rate with Selenious Acid Concentration.

$$-\frac{d(H_2O_2)}{dt} = \left[m\ (H_2O_2) + n\ (H_2O_2)^2\right](H_2SeO_3)\left[\frac{h}{(H^+)} + 1\right]$$

The first expression was finally selected because its use led to a final rate law which described all of the data. For the first expression, therefore, the constants k_2' and k_2'' were evaluated from Figure 7 and 8. The same value 0.0055 was obtained for each constant.

That the rate expression was still not complete was made evident by an experiment in which the perchloric acid was replaced by selenic acid. When the rate calculated from the terms already determined was subtracted from the hydrogen peroxide decomposition rate, the resultant rate was found to be proportional only to the selenious acid and hydrogen peroxide concentrations. This is shown in Table 2. It was assumed that there was also a first order dependence of the rate upon selenic acid. This term was found to be not enough to account for the extra decomposition of hydrogen peroxide at low acidities. Therefore an inverse dependence upon hydrogen-ion was introduced into the term. The complete rate expression for the hydrogen peroxide decomposition was then written as

$$-\frac{d(H_2O_2)}{dt} = \frac{k_2'(H_2O_2)(H_2SeO_3)}{(H^+)} + k_2''(H_2O_2)^2(H_2SeO_3) + \frac{k_2'''(H_2SeO_3)(HSeO_4^-)(H_2O_2)}{(H^+)}$$

The validity of this expression has been tested by comparing rates calculated from it with the actual experimental rates of reactions in which the hydrogen-ion concentration was low. Under this condition the terms depending upon the hydrogen-ion concentration would make large contributions to the overall rate. A typical comparison is shown in Table 3. The agreement between calculation and experiment

Table 2

Evaluation of Rate Constant k_2'''

Time (hours)	(H_2SeO_3) m/l	(H_2O_2) m/l	(H_2SeO_4) m/l	(H^+) m/l	Subtracted Rate m/l-hr.	$\frac{\text{Rate}}{(H_2O_2)(H_2SeO_3)}$
0	.486	2.50	1.717	1.717	.0305	.0251
5	.444	2.21	1.761	1.761	.0249	.0253
10	.410	2.02	1.794	1.794	.0193	.0233
15	.383	1.85	1.820	1.820	.0161	.0227
20	.361	1.71	1.842	1.842	.0136	.0220
25	.343	1.59	1.860	1.860	.0119	.0218
30	.328	1.49	1.875	1.875	.0102	.0209
50	.284	1.17	1.919	1.919	.0079	.0238
60	.267	1.05	1.936	1.936	.0071	.0253
100	.225	.75	1.978	1.978	.0037	.0219

is quite good considering the ranges within which the concentrations of the reactants varied.

Table 3

Comparison of Calculated and Experimental Rates

(H_2O_2) m/l	(H_2SeO_3) m/l	(H^+) m/l	(H_2SeO_4) m/l	Calculated Rate m/l-hr.	Experimental Rate
2.47	.485	.253	0	.0423	.0422
2.15	.330	.408	.155	.0245	.0241
1.99	.278	.460	.207	.0186	.0190
1.87	.249	.489	.236	.0153	.0159
1.77	.228	.510	.257	.0132	.0135
1.69	.206	.532	.279	.0113	.0118
1.62	.191	.547	.294	.0099	.0106
1.56	.178	.560	.307	.0087	.0097
1.50	.166	.572	.319	.0077	.0087
1.45	.157	.581	.328	.0071	.0080
1.40	.149	.589	.336	.0065	.0073
1.36	.142	.596	.343	.0059	.0069
1.32	.137	.601	.348	.0055	.0065
1.25	.129	.609	.356	.0049	.0059
1.18	.123	.615	.362	.0043	.0053
1.06	.119	.619	.366	.0036	.0045

3. Homogeneity of the reactions

The homogeneity of the reactions was tested by variation of both the magnitude and type of solid surface containing the reaction mixtures. The rates obtained from the reactions carried out in pyrex vessels, to which pyrex glass helices had been added to increase the surface area sixteen-fold, were not significantly different from those obtained under normal conditions. Similarly, there was no significant difference in the rates when the reactions were carried out in polyethylene containers. A comparison of typical rates obtained is shown in Table 4.

Table 4

Comparison of Surface Effects

Type of Surface	(H_2SeO_3) m/l	(H_2SeO_4) m/l	(H_2O_2) m/l	$(HClO_4)$ m/l	(H^+) m/l	$\frac{d(H_2SeO_3)}{dt}$ m/l-hr	k_1	$\frac{d(H_2O_2)}{dt}$
Pyrex	.407	.075	2.21	1.772	1.847	.00529	.0267	.0165
Pyrex (16-fold increase)	.422	.117	1.86	1.712	1.829	.00373	.0275	.0162
Polyethylene	.439	.113	2.22	1.590	1.703	.00567	.0225	.0210

Two reactions were carried out in the presence of a small amount of bright platinum sheet. The gross hydrogen peroxide disappearance rate was increased by a factor of four over the rate obtained without the platinum. On the other hand, the selenious acid oxidation rate was different by only 15% from the rate without the platinum and only 11% from the average as shown in Figure 5. Since this is within the range of experimental accuracy, the selenious acid oxidation rate may be considered to be independent of the presence of platinum. An example of the results obtained is shown in Table 5.

Table 5

Effect of Platinum on Reaction

Pt	(H_2SeO_3)	(H_2SeO_4)	(H_2O_2)	$(HClO_4)$	(H^+)	$\frac{d(H_2SeO_3)}{dt}$	k_1	$\frac{d(H_2O_2)}{dt}$
	m/l	m/l	m/l	m/l	m/l			
No	.482	0	2.47	1.772	1.772	.00890	.0275	.0203
Yes	.517	0	2.43	1.706	1.706	.00896	.0235	.0817
Yes	.114	0	2.43	1.688	1.688	0	-----	.0294

4. Effect of iron(III)

Iron(III) acts as a catalyst in the homogeneous decomposition of acidic solutions of hydrogen peroxide. It was found that selenious acid and selenic acid both decreased the effectiveness of the catalysis. Sulfate has been reported to have an effect similar to that of selenic acid[30] but the magnitude of the effect does not appear to be as great although no direct comparison has been made. The results are presented graphically in Figure 10 as plots of the logarithms of hydrogen peroxide concentrations versus time. The first order reaction rate constant was decreased by a factor of nine by the presence of 0.25 M selenious acid and by a factor of ninety by the presence of both 0.25 M selenious acid and 1.7 M selenic acid.

Within the range of experimental accuracy the rate constant of the oxidation of selenious acid by hydrogen peroxide was unaffected by the presence of iron(III). The results are shown in Table 6.

Table 6

Effect of Iron(III) on Selenious Acid Oxidation

(Fe^{III}) m/l	(H_2SeO_3) m/l	(H_2SeO_4) m/l	(H_2O_2) m/l	$(HClO_4)$ m/l	(H^+) m/l	$\frac{d(H_2SeO_3)}{dt}$	k_1
0	.548	0	.499	1.640	1.640	.00254	.0278
.00052	.498	0	.494	1.724	1.724	.00213	.0299

5. Temperature dependence

All data mentioned previously in this section were taken at 67.7°C. However, a limited number of experiments were

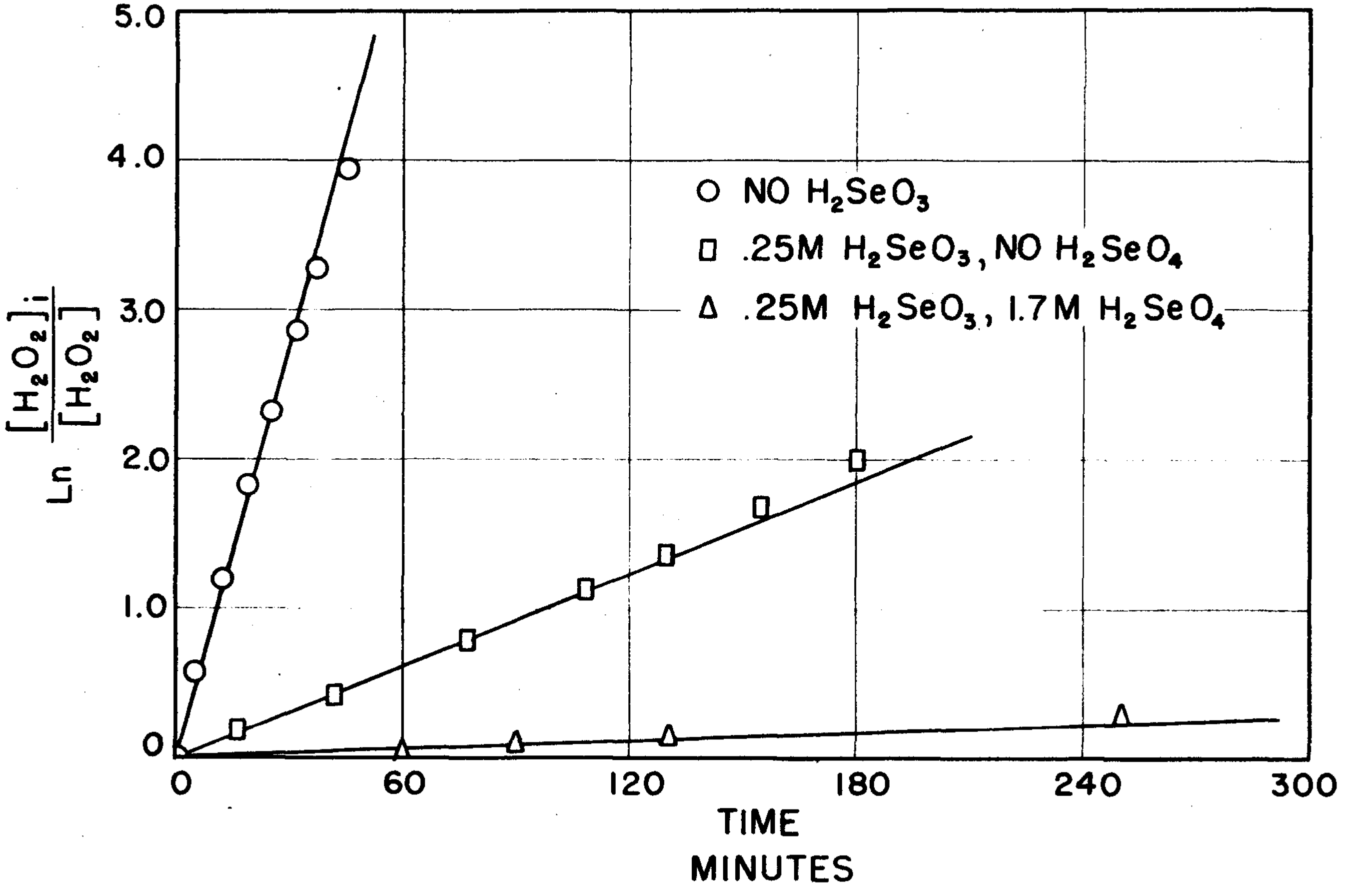


Figure 10. Inhibition Effect of Selenious and Selenic Acids on the Reaction of Iron(III) with Hydrogen Peroxide.

carried out at 75.0°C and at 82.3°C. With the assumption that the rate expression determined at 67.7°C was valid at higher temperatures, the values of k_2', k_2'', and k_2''' at the two higher temperatures were obtained in the following manner. Three experiments were performed at each of these higher temperatures, one at low acidity, one at high acidity, and one at high selenic acid concentration. The rates obtained at the beginning of each of these experiments are listed in Table 7. The parameters k_2' and k_2'' were evaluated from the initial rates of the hydrogen peroxide decompositions in the high acidity and low acidity reactions since only the hydrogen-ion concentration was significantly different and since no selenic acid was present initially. Then these parameters were employed to calculate the contribution of the respective rate terms to the hydrogen peroxide decomposition rate in the high selenic acid reaction. When these quantities were subtracted from the hydrogen peroxide decomposition rates at certain time intervals in the high selenic acid reaction, each of the resultant amounts was divided or multiplied by the appropriate concentrations to give the quantity k_2'''. The constancy of the values of k_2''' obtained throughout the reaction was used as a measure of the validity of the rate law. Satisfactory constancy was obtained at 75.0°C, but no constancy was obtainable at

Table 7

Data from Reactions Carried Out at Higher Temperatures

Temp. in °C	Reaction Number	Time (hours)	(H_2SeO_3) m/l	(H_2O_2) m/l	$(HClO_4)$ m/l	(H_2SeO_4) m/l	(H^+) m/l	$\frac{d(H_2SeO_3)}{dt}$ m/l-hr.	$\frac{d(H_2O_2)-d(H_2SeO_3)}{dt}$ m/l-hr.
75.0	28	0	0.540	2.44	1.704	0	1.704	0.0170	0.0519
75.0	29	0	0.496	2.43	0.558	0	0.558	0.0471	0.0573
75.0	30	0	0.578	2.48	0	1.690	1.690	0.0243	0.0889
82.3	31	0	0.552	2.43	1.681	0	1.681	0.0333	0.0933
82.3	32	0	0.495	2.44	0.551	0	0.551	0.0860	0.1445
82.3	33	0	0.597	2.46	0	1.665	1.665	0.0430	0.1378

82.3°C. It seems likely then that the rate law determined at 67.7°C does not hold at 82.3°C.

The values of constants obtained at the various temperatures are listed in Table 8. The empirical activation energy of the selenious acid oxidation was calculated to be 16,200 kilocalories per mole.

Table 8

Values of Rate Constants

Temperature in °C	k_1 1/m-hr.	k_2' hr.$^{-1}$	k_2'' $1^2/m^2$-hr.	k_2''' 1/m-hr.
67.7	.0265	.0055	.0055	.024
75.0	.044	.0038	.0163	.024
82.3	.079	no constants obtained		

6. Radioactive tracer experiment

Selenious acid containing a small amount of Se^{75} radioactive tracer was introduced into a mixture of selenic acid, hydrogen peroxide, and water at 67.7°C. The specific activity of the selenious acid was measured immediately and at later times. The results are presented

Table 9

Radioactive Tracer Measurements

Time (hours)	(H_2SeO_3) m/l	(H_2O_2) m/l	(H_2SeO_3) m/l	Specific Activity of Selenious Acid (-ray counts/ mg Se)
0	.115	4.02	1.36	1.55±.03
192	.05	1.13	1.42	1.48±.03
336	.03	.84	1.44	1.46±.03

in Table 9. No exchange of selenium between selenious and selenic acids was in evidence.

IV. DISCUSSION

A. Evidence Favoring a Free Radical Reaction

Evidence for the existence of the free radicals OH and HO_2 in peroxide systems has been reviewed by Weiss[31] and Uri.[14] They may be expected, therefore, in a selenious acid-hydrogen peroxide system.

Addition of selenious acid to an aqueous acidic hydrogen peroxide solution at first decreases the rate of decomposition of the hydrogen peroxide, but further addition of the selenious acid then increases the rate of disappearance of the hydrogen peroxide. This inhibition effect can be explained by the existence of a free radical intermediate which is formed by a reaction of either OH or HO_2 with selenious acid but which is also involved in a chain termination reaction which is faster than the original chain termination step.

The hydrogen peroxide decomposition in the presence of selenious acid is accelerated by the presence of a small amount of bright platinum. The selenious acid oxidation, on the other hand, is unaffected by the platinum. Thus if the function of the platinum is to increase the formation of free radicals as Weiss suggests,[20] these facts indicate that the catalytic decomposition of hydrogen peroxide by selenious acid is a free radical process while the oxidation of selenious acid by hydrogen peroxide is not.

The iron(III) catalysis of the decomposition of hydrogen peroxide is inhibited by the presence of either selenious acid or selenic acid. This suggests but does not require the presence of a selenium containing free radical which would be involved in a chain termination step.

B. The Selenious Acid Reaction

The rate equation for the oxidation of selenious acid by hydrogen peroxide has been shown to be

$$-\frac{d(H_2SeO_3)}{dt} = \frac{k_1(H_2SeO_3)^2(H_2O_2)}{(H^+)}$$

Several mechanisms which satisfy this law are given below.

$$\left.\begin{array}{lcl} H_2SeO_3 + H_2O_2 & \rightleftharpoons & HOOSeO_2H + H_2O \\ HOOSeO_2H & \rightleftharpoons & H^+ + HOOSeO_2^- \\ HOOSeO_2^- + H_2SeO_3 & \longrightarrow & H_2SeO_3 + HSeO_4^- \end{array}\right\} \quad (I)$$

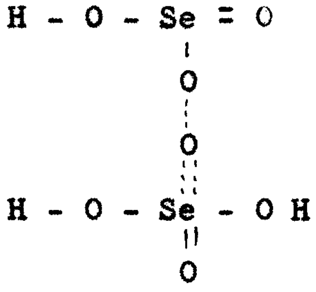
$$\left.\begin{array}{lcl} 2H_2SeO_3 & \rightleftharpoons & HSe_2O_5^- + H^+ + H_2O \\ HSe_2O_5^- + H_2O_2 & \longrightarrow & HSeO_4^- + H_2SeO_3 \end{array}\right\} \quad (II)$$

$$2H_2SeO_3 + H_2O_2 \rightleftharpoons H_2Se_2O_6 + H_2O \qquad \text{(III)}$$
$$H_2Se_2O_6 + OH^- \longrightarrow HSeO_4^- + H_2SeO_3$$

A free radical mechanism for this particular reaction step was not considered likely in view of the failure of the bright platinum to accelerate the reaction.

Both Shilov and Stepanova[18] with the nitrous acid-hydrogen peroxide reaction and Halperin and Taube[26] with the sulfurous acid-hydrogen peroxide reaction have proposed mechanisms involving monoperoxy acids.

Schemes I and III might proceed through similar transition states



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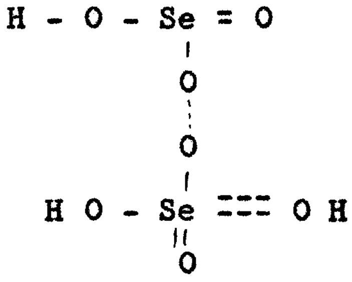
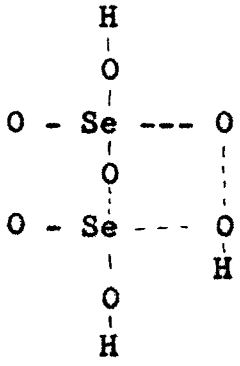


III

while scheme II will have a somewhat different one.



II

Since it is difficult to distinguish between these systems, each of the above mechanisms appear equally well to explain the data. In any case the transition state would seem to have the composition $H_3Se_2O_7$.

C. The Hydrogen Peroxide Decomposition

The total hydrogen peroxide decomposition rate is given by the expression

$$-\frac{d(H_2O_2)}{dt} = \frac{k_2'(H_2SeO_3)(H_2O_2)}{(H^+)} + k_2''(H_2SeO_3)(H_2O_2)^2 + \frac{k_2'''(HSeO_4^-)(H_2SeO_3)(H_2O_2)}{(H^+)} .$$

A non-free radical mechanism may be formulated to account for the above rate expression by employing various reactions and equilibria to form the proper transition states. The inhibition of the spontaneous surface catalyzed decomposition of hydrogen peroxide by selenious acid can be explained by the assumption that the active surface is poisoned by adsorption of selenious acid. The addition of platinum, however, would catalyze this surface dependent reaction.

The lack of exchange of selenium between selenious and selenic acids precludes the possibility of reduction of selenic acid to selenious acid as a mechanism step. This is certainly in line with the general lack of reactivity of selenic acid. It seems, though, that a selenium-containing reaction intermediate is required which may be formed from but later reverts to selenious acid. Both processes would involve hydrogen peroxide or a free radical formed from it.

For reasons given previously, a free radical mechanism is preferred in explaining the catalytic decomposition of hydrogen peroxide by selenious acid.

If a free radical mechanism is operable in the surface catalyzed reaction, it may well take the following course

$$\begin{array}{rcll}
 & H_2O_2 \longrightarrow & 2\,OH & k_{I} \quad (1) \\
OH & + H_2O_2 \longrightarrow & HO_2 + H_2O & k_{II} \quad (2) \\
O_2^- & + H_2O_2 \longrightarrow & OH^- + OH + O_2 & k_{III} \quad (3) \\
OH & + HO_2 \longrightarrow & H_2O + O_2 & k_{IV} \quad (4)
\end{array}$$

Experimentally the reaction is first order in hydrogen peroxide, but the above mechanism would account for this result if the chain initiation step were independent of the hydrogen peroxide concentration.

Consideration of $HSeO_3$ as a reactive intermediate leads to an additional chain initiation step.

$$HSeO_3^- + H_2O_2 \longrightarrow OH + HSeO_3 + OH^- \quad k_{V} \quad (5)$$

This, together with the chain carrying steps

$$OH + H_2SeO_3 \longrightarrow HSeO_3 + HO_2 \qquad k_{VI} \quad (6)$$

$$HOOSeO_2H + OH \longrightarrow HO_2 + H_2SeO_3 \qquad k_{VII} \quad (7)$$

$$HSeO_3 + H_2O_2 \longrightarrow H_2SeO_3 + HO_2 \qquad k_{VIII} \quad (8)$$

and the chain termination step

$$OH + HSeO_3 \longrightarrow H_2SeO_4 \qquad k_{IX} \quad (9)$$

constitute a chain mechanism which explains the kinetics observed.

Several equilibria are required to complete the system.

$$H_2SeO_3 + H_2O_2 \rightleftharpoons HOOSeO_2H + H_2O \qquad K_1$$

$$H_2SeO_3 \rightleftharpoons H^+ + HSeO_3^- \qquad K_a$$

$$HOOSeO_2H \rightleftharpoons H^+ + HOOSeO_2^- \qquad K_s$$

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad K_h$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad K_o$$

Application of the usual steady state approximation for free radical concentrations leads to the following equations

$$\frac{d(OH)}{dt} + 2\,R_1 - R_2 + R_3 - R_4 + R_5 - R_6 - R_8 - R_9 = 0$$

$$\frac{d(HO_2)}{dt} = R_2 - R_3 - R_4 + R_7 + R_8 = 0$$

$$\frac{d(HSeO_3)}{dt} = R_5 + R_6 - R_7 - R_9 \qquad = 0$$

in which R_n is the rate of the nth reaction. The chains are assumed to be long and the rates of the chain carrying steps are considered to be fast with respect to those of the chain initiating and chain terminating steps. The steady state concentration of each of the free radicals is obtained by simultaneous solution of the above three rate equations. Since the consumption of peroxide according to the free radical mechanism is

$$\frac{d(H_2O_2)}{dt} = 2\,R_2 + 2\,R_7 + 2\,R_8$$

the rate law for the decomposition of hydrogen peroxide becomes

$$-\frac{d(H_2O_2)}{dt} = \left\{2k_{II}(H_2O_2) + 2k_{VII}K_1(H_2SeO_3)(H_2O_2) + 2k_{VI}k_{VIII}K_a\frac{(H_2SeO_3)}{(H^+)}\right\}K'$$

in which K' equals

$$\sqrt{\frac{k_I(H^+)(H_2O_2) + k_VK_a(H_2SeO_3)(H_2O_2)^2}{(H^+)\left\{\frac{k_{II}k_{IV}}{k_{III}}(H_2O_2) + (H_2SeO_3)\left[\frac{k_{IV}k_{VII}K_1}{k_{III}}(H_2O_2) + \frac{k_{IV}k_{VI}K_a}{k_{III}(H^+)} + \frac{k_{IX}k_{VI}K_a}{k_{VIII}(H^+)}\right]\right\}}}$$

When no selenious acid is present the rate law is simply first order with respect to hydrogen peroxide concentration, but for small amounts of selenious acid the peroxide decomposition becomes

$$-\frac{d(H_2O_2)}{dt} = 2k_{II}\,(H_2O_2)\sqrt{\frac{k_I(H_2O_2)}{\dfrac{k_{II}\,k_{IV}}{k_{III}}(H_2O_2) + \dfrac{k_{VI}\,k_{IX}\,K_a}{k_{VIII}K_h}\,(H_2SeO_3)}}$$

This function is fitted to the experimental points and plotted as the lower dotted line in Figure 9. At high selenious acid concentration, however, (1), (2), and (4) become unimportant compared to (5), (8), and (9) and the expression becomes

$$-\frac{d(H_2O_2)}{dt} = \left\{\frac{2k_{VI}k_{VIII}K_a(H_2SeO_3)}{(H^+)} + 2k_{VII}K_1(H_2SeO_3)(H_2O_2)\right\}\sqrt{\frac{k_V\,k_{VIII}}{k_{VI}k_{IX}}}(H_2O_2).$$

A rate term containing the selenic acid dependence can be introduced with the proposal of two more reaction steps

$$Se_2O_6^{=} + OH \longrightarrow Se_2O_6^{-} + OH^{-} \qquad k_X$$

$$Se_2O_6^{-} + HO_2^{-} \longrightarrow Se_2O_6^{=} + HO_2 \qquad k_{XI}$$

together with the equilibria

$$HSeO_4^{-} + H_2SeO_3 \rightleftharpoons HSe_2O_6^{-} + H_2O \qquad K_I$$

$$HSe_2O_6^{-} \rightleftharpoons H^+ + Se_2O_6^{=} \qquad K_J$$

The complete expression for the hydrogen peroxide decomposition rate then becomes

$$- \frac{d(H_2O_2)}{dt} = \Big\{ 2k_{\mathrm{II}}(H_2O_2) + 2k_{\mathrm{VII}}K_1(HSeO_3)(H_2O_2)$$

$$+ \frac{2k_{\mathrm{VI}}k_{\mathrm{VIII}}K_a(H_2SeO_3}{(H^+)} + \frac{2k_{\mathrm{X}}K_{\mathrm{I}}\ K_{\mathrm{J}}\ (H_2SeO_3)(HSeO_4^-)}{(H^+)} \Big\} K''$$

where K" equals

$$\sqrt{\frac{k_{\mathrm{I}}(H^+)(H_2O_2) + k_{\mathrm{V}}K_a(H_2SeO_3)(H_2O_2)^2}{(H^+)\left\{\frac{k_{\mathrm{II}}k_{\mathrm{IV}}}{k_{\mathrm{III}}}(H_2O_2) + (H_2SeO_3)\left[\frac{k_{\mathrm{IV}}k_{\mathrm{VII}}K_1}{k_{\mathrm{III}}}(H_2O_2) + \frac{k_{\mathrm{II}}k_{\mathrm{VI}}K_a}{k_{\mathrm{III}}(H^+)} + \frac{k_{\mathrm{IV}}k_{\mathrm{X}}K_{\mathrm{I}}\ K_{\mathrm{J}}}{k_{\mathrm{III}}\ (H^+)}(HSeO_4^-) + \frac{k_{\mathrm{VI}}k_{\mathrm{IX}}K_a}{k_{\mathrm{VIII}}}\right]\right\}}}\ .$$

An analogous system may be set up by employing the free radicals OH, HO_2, and $HSeO_2$. In this treatment the $HSeO_2$ radical is a reducing agent (in contrast to the $HSeO_3$ radical) while the OH and HO_2 radicals have slightly different roles. The kinetic expression obtained is identical in form to the one already calculated for $HSeO_3$. It does not explain satisfactorily the selenic acid dependent term, however, in the hydrogen peroxide decomposition rate expression.

V. SUMMARY

1. The rates of disappearance of selenious acid and hydrogen peroxide have been measured in aqueous acidic solutions containing the two species. Temperature variation of these rates has been observed between 67.7°C and 82.3°C.

2. The following rate law has been determined for the oxidation of selenious acid by hydrogen peroxide:

$$-\frac{d(H_2SeO_3)}{dt} = \frac{k_1(H_2SeO_3)^2(H_2O_2)}{(H^+)} .$$

3. The decomposition of hydrogen peroxide in aqueous acidic solution has been shown to be inhibited by the presence of a small amount of selenious acid. Another mode of decomposition of hydrogen peroxide has been shown to exist and has been found to be first order in selenious acid. At least four rate terms were required to account for the decomposition rate of the peroxide.

4. The evidence indicated that the reactions which involved selenious acid were homogeneous.

5. The selenious acid oxidation is believed to be non-free radical in character while the extra hydrogen

peroxide decomposition which accompanies it is believed to proceed through a free radical chain mechanism.

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