reaching the catalyst either is oxidized or reduced while in the homogeneous case, the third choice of not reacting at all, is open.

The relationship for the diffusion controlled heterogeneous case can easily be seen using equation (3). The composition of H_2O_2 diffusing in at any time is $N_p f_d$. According to equation (3) this disproportionates as

$$\frac{N_g}{N_p f_d} = \frac{2}{1 + f_r/f_0}$$

whence N_g/N_p for the decomposition of an infinitesimal amount $= 2\ f_d/(1 + f_r/f_0)$. As $x \rightarrow 0$, $N_g/N_p^0 \rightarrow 2f_d/(1 \times f_r/f_0)$. At complete decomposition, as the homogeneous case, $N_g^1/N_p^\circ = 2/(1 + f_r/f_0)$. Measurements at both extremes permit f_d and f_r/f_0 to be determined.

The data we have obtained for solids are incomplete and are for complete decomposition. In view of the fact that f_0 for most substances is close to unity, it seems safe to conclude that for Pt, f_r is also close to unity, and that for MnO_2, it is lower but still higher than for Fe^{++} or Sn^{++}.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Reaction of Thiosulfate Ion and Selenious Acid

BY C. H. SORUM AND JOHN O. EDWARDS[1]

The kinetics and mechanism of the oxidation of thiosulfate ion by hydrogen selenite ion have been investigated in the *p*H range from 4.2 to 6.4 by means of the change in thiosulfate concentration and *p*H with time. The reaction starts with the rate law, $-\ d[S_2O_3^=]/dt = k_5[HSeO_3^-][S_2O_3^=]^2[H^+]^2$. However, selenopentathionate ion is formed and this ion acts as a catalyst which greatly increases the reaction rate above *p*H 4.5. The catalyzed reaction was found to have the rate law $-\ d[S_2O_3^=]/dt = k_3[HSeO_3^-]^{1/2}[S_2O_3^=]^{3/2}[Se(S_2O_3)_2^=]^{1/2}[H^+]^{1/2}$. Some observations on the rate of formation of colloidal selenium showed that it is dependent to a large degree on the concentration of selenopentathionate and less so on the thiosulfate concentration. The rate of decomposition of selenopentathionate is greatly increased by sunlight.

Introduction

As part of a series of studies on the use of the *p*H meter in the determination of reaction mechanisms, it was decided to investigate the oxidation of thiosulfate ion to tetrathionate ion by selenious acid. This reaction, which is essentially instantaneous in one normal acid, proceeds at a measurable speed above *p*H 4. While the reaction kinetics are complex, and complete elucidation of the mechanism is not at hand, some of the results are clear-cut. These will be presented here.

When the concentration of thiosulfate ion is plotted as a function of time for the reaction between thiosulfate and hydrogen selenite ion at initial *p*H values of 4.20, 4.94 and 5.10, curves 1, 2 and 3, respectively, of Fig. 1 are obtained. When the *p*H of the reaction mixture is plotted as a function of time, curves 1, 2 and 3 of Fig. 2 are obtained for the same experiments as shown in Fig. 1. The similarity of number 1 curves in each figure, and of the number 2 curves, and of the number 3 curves, indicates that the *p*H change complements the change in thiosulfate concentration. Hence the *p*H change serves as an additional measure of the rate of the reaction despite the logarithmic nature of the *p*H function.

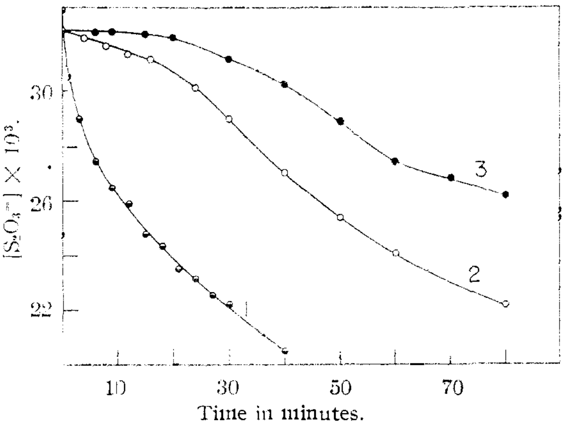

Fig. 1.—Change in thiosulfate ion concentration with time as a function of initial *p*H: $[HSeO_3^-] = [S_2O_3]$; ionic strength = 0.210 ± 0.015; t = 30.0°. Initial *p*H values are 4.20, 4.94 and 5.10 for 1, 2 and 3, respectively.

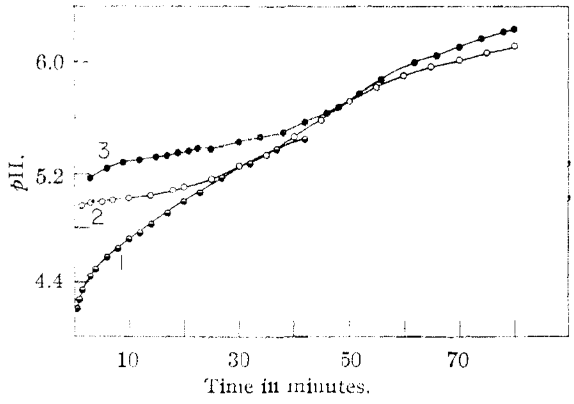

Fig. 2.—Change in *p*H for the three experiments of Fig. 1.

The differences in the shapes of the curves in each figure demonstrate that the *p*H of the system has a pronounced effect on both the rate and mechanism of the reaction. The upper half of curves 2 and 3 in Fig. 1 and the corresponding lower half of curves

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[1] Research Assistant, 1949–1950.

2 and 3 in Fig. 2 are representative of an autocatalyzed reaction; the reaction starts out slowly and then proceeds at accelerated speed. By contrast with these curves, curve 1 (of both figures) appears to be a typical concentration-dependent rate with little indication of autocatalysis. It is evident, therefore, that the primary process is speeded up greatly as the hydrogen ion concentration is increased and that the rate of the secondary reaction is not increased as much.

In an effort to provide kinetic laws and mechanisms that will account for this behavior, rates were determined at different reactant concentrations, *p*H values, temperatures and ionic strengths. The first stage of the reaction, which is referred to as the primary process, was probed by studying the reaction from its inception up to the point where 2 to 8% of the initial thiosulfate had been consumed. The second stage, referred to as the secondary process, was investigated by observing the changes that took place after the reaction mixture had been allowed to stand for a period ranging from 10 to 30 minutes and by the usual kinetic procedures in a *p*H range where the primary reaction did not take place. Finally, the decomposition of selenopentathionate ion, which is thought to be the reactive intermediate, was studied.

Experimental

All chemicals employed were reagent grade except the sodium selenite which was Fisher C.P. grade. All water was redistilled from alkaline permanganate.

For determination of the *p*H, a Beckman Model G meter was used, and National Technical Laboratory Buffer (*p*H 7.00 ± 0.01) was used for standardization of the glass electrode. On identical experiments, the variation was found to be ± 0.02 *p*H unit.

Solutions were kept in glass-stoppered bottles in a constant temperature bath which was maintained at the desired temperature to ± 0.1°. All pipets were marked and used for only one reagent. The thiosulfate solutions were standardized by the dichromate method. Selenite concentrations were determined by the Norris and Fay method,[2] using the standard thiosulfate solution. Triiodide solutions were also standardized with this solution.

The reaction vessel was usually a Florence flask; on shorter runs, a beaker was used. The selenite solution, adjusted to the desired *p*H and salt content, was placed in the reaction vessel. Thiosulfate solution was then added, with vigorous stirring to ensure complete mixing. The thiosulfate was added last in order to minimize decomposition in the slightly acid solution. Aliquots were withdrawn at intervals and quenched into an excess of the standard triiodide solution and a large volume of water; the residual iodine was back-titrated immediately with thiosulfate and starch indicator. Reproducible results were obtained only if the amount of iodine was very slightly in excess, as iodine slowly oxidizes tetrathionate to sulfate and as selenopentathionate also caused a slow disappearance of excess iodine. Control experiments showed that hydrogen selenite ion did not oxidize iodide under the conditions of the titration.

A separate 400-ml. beaker was employed for continuous *p*H measurement during each experiment. After time was allowed for complete mixing, an aliquot from the reaction vessel was run into the beaker and readings were taken.

Within the *p*H range studied, the tetravalent selenium exists as the hydrogen selenite ion $HSeO_3^-$. The values employed for the dissociation constants are 2.4×10^{-3} and 4.8×10^{-9}.[3] For the buffer, potassium hydrogen phthalate was used.

The Primary Reaction.—The stoichiometry of the reaction in strongly acid solution is represented by the equation[2]

$$H_2SeO_3 + 4S_2O_3^{=} + 4H^+ \longrightarrow Se(S_2O_3)_2^{=} + S_4O_6^{=} + 3H_2O$$

Several of our kinetic experiments were followed to 75% of completion and this stoichiometry was found to hold to better than 90%. In the presence of base or excess thiosulfate, the selenopentathionate is decomposed to give free selenium and tetrathionate. Foss[4] has recently investigated the chemistry of selenopentathionate and related compounds.

Based on data to be presented, the following mechanism for the primary reaction is postulated

$$HSeO_3^- + H^+ \rightleftarrows H_2SeO_3 \qquad \text{(fast)}$$

$$H_2SeO_3 + S_2O_3^{=} \rightleftarrows SeO_2{\cdot}S_2O_3^{=} + H_2O \ \text{(fast)}$$

$$H^+ + SeO_2{\cdot}S_2O_3^{=} \rightleftarrows HSeO_2{\cdot}S_2O_3^- \qquad \text{(fast)}$$

$$HSeO_2{\cdot}S_2O_3^- + S_2O_3^{=} \longrightarrow SeO{\cdot}(S_2O_3)_2^{=} + OH^- \text{(rate)}$$

$$SeO{\cdot}(S_2O_3)_2^{=} + S_2O_3^{=} + H^+ \longrightarrow HOSeS_2O_3^- + S_4O_6^{=} \qquad \text{(fast)}$$

$$HOSeS_2O_3^- + S_2O_3^{=} \longrightarrow Se(S_2O_3)_2^{=} + OH^- \ \text{(fast)}$$

since the observed rate law is

$$-\,d[S_2O_3^{=}]/dt = k_5[HSeO_3^-][S_2O_3^{=}]^2[H^+]^2$$

in the initial stage of the reaction.

In buffered medium, the dependences of the rate on the concentrations of thiosulfate and of hydrogen selenite were studied. In view of the autocatalysis, these experiments were carried out at *p*H 4.35 where the primary mechanism is fast compared to the secondary process. In Table I, data on the kinetics of the primary reaction are presented. The results show conclusively that the rate is second order in thiosulfate concentration and first order in hydrogen selenite concentration. Other kinetic experiments supplemented these data.

TABLE I

PRIMARY RATE DEPENDENCE ON REACTANT CONCENTRATIONS

*p*H 4.35; [buffer] = 0.11 *M*; [NaCl] = 0.79 *M*; $t = 29.95°$

A. Dependence on thiosulfate; $[HSeO_3^-] = 2.58 \times 10^{-3}$ *M*

$[S_2O_3^{=}] \times 10^3$ *M*	$S \times 10^5$ [a]	$S \times 10/[S_2O_3^{=}]^2$
6.38	1.24	3.03
12.8	4.69	3.00
25.5	19.9	3.06

B. Dependence on hydrogen selenite; $[S_2O_3^{=}] = 12.8 \times 10^{-3}$ *M*

$[HSeO_3^-] \times 10^3$ *M*	$S \times 10^5$ [a]	$S \times 100/[HSeO_3^-]$
1.29	2.91	2.24
2.58	4.69	1.80
6.45	11.6	1.79
12.9	28.5	2.21

[a] *S* is defined as the absolute value of the rate of change of $[S_2O_3^{=}]$ with time.

The dependence of the rate on the hydrogen ion concentration was studied by observing the change in the third-order rate constant k_x, defined as

$$-\,d[S_2O_3^{=}]/dt = k_x[S_2O_3^{=}]^2[HSeO_3^-]$$

when the *p*H was varied. The values of k_x were determined graphically, and some typical results

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[2] (a) J. F. Norris and H. Fay, *Am. Chem. J.*, **18**, 703 (1896); **23**, 119 (1900). (b) W. C. Coleman and C. R. McCroskey, *Ind. Eng. Chem., Anal. Ed.*, **8**, 196 (1936).

[3] D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 331.

[4] O. Foss, THIS JOURNAL, **70**, 421 (1948); *Acta Chem. Scand.*, 435, 708, 1385 (1949); *ibid.*, **4**, 866, 1241 (1950).

are presented in Fig. 3. Within the range of *p*H from 4.2 to 5.3, the rate is second order in hydrogen ion concentration with little deviation aside from ionic strength effects.

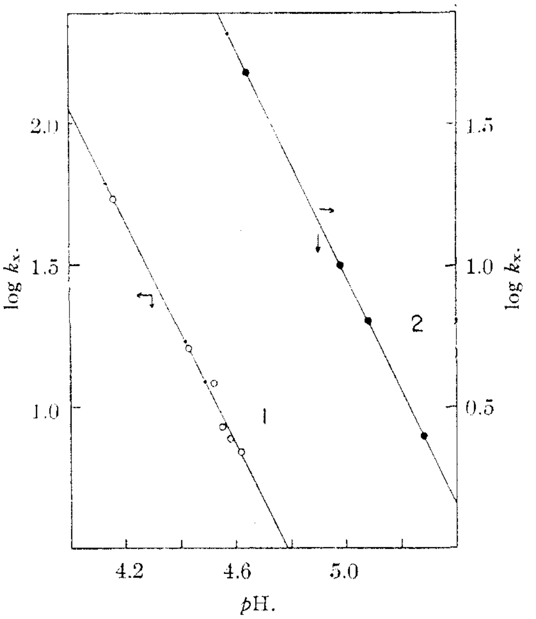

Fig. 3.—Variation of third-order rate constants k_x with *p*H: line 1, t = 25.0°, ionic strength = 0.06 ± 0.03; line 2, t = 30.0°, ionic strength = 0.210 ± 0.015.

In Table II, data from seven experiments are presented in order to show the effect of ionic strength on the rate. These, and nine other experiments at 25° but with varying reactant concentrations, showed that the primary rate is increased by additions of inert salt. The values of log k_5 fell between 10.53 and 10.93 and the plot of log k_5 against the square root of ionic strength had a slope of about +0.9, although the points showed some scattering and the best loci were decidedly curved away from the ordinate. Potassium chloride and potassium bromide were the inert salts employed; the buffer concentration was also varied in some of the experiments.

TABLE II

EFFECT OF IONIC STRENGTH ON THE PRIMARY RATE

$t = 25.0°$; $[S_2O_3^=] = [HSeO_3^-] = 16.4 \times 10^{-3}$ *N*

k_x[a]	Average *p*H	log k_5[b]	Ionic strength
38.4	4.52	10.62	0.061
24.6	4.58	10.55	.065
41.6	4.51	10.64	.078
45.6	4.49	10.64	.095
34.2	4.56	10.65	.099
95.2	4.42	10.82	.230
135	4.40	10.93	.399

[a] Units of k_x are liter ^{2} mole^{-2} min.$^{-1}$. [b] Units of k_5 are liter^4 mole^{-4} min.$^{-1}$.

In Table III, data on the temperature dependence of the primary reaction are presented. Correction for the change in the observed *p*H was made by calibration of the glass electrode at each temperature with the standard buffer. The over-all heat of activation is 10.0 ± 1.0 kcal. mole^{-1}.

TABLE III

EFFECT OF TEMPERATURE ON THE PRIMARY RATE

Ionic strength = 0.44; $[S_2O_3^=] = [HSeO_3^-] = 1.70 \times 10^{-2}$ *N*; [buffer] = 9.7×10^{-2} *M*

log kx	Average *p*H	$k_5 \times 10^{-10}$	Temp., °C.
1.003	4.81-4.82	4.3	15.9
1.206	4.83	7.4	25.0
1.342	4.89	13.2	35.0

The rate equation for the primary reaction is fifth order. In view of the improbability of a collision process, involving most or all of these ions, being rate-determining and since the results fit well into those found for other inorganic oxyanion reactions with electron donors,[5] we postulate the mechanism given earlier. Further evidence for the existence of a reasonably stable intermediate is found in the large rate constant and the sizeable activation energy. In order to be consistent with the rate of molecular collisions, it is necessary to assume that the complex $HSeO_2 \cdot S_2O_3^-$ has an association constant which is greater than one. Of course, other complexes may be considered. We have postulated this one for it can be described as a salt formed by displacement of water from selenious acid by thiosulfate ion. Other confirmatory evidence is found in the nature of the final product, selenopentathionate ion. In the terminology of Foss,[4] this species may be considered a compound of divalent selenium.

A similar type of reaction complex was proposed by Duke[6] in order to explain the kinetics of the oxidation of acetone by selenious acid. In that case, the reaction proceeds by disproportionation of the complex and not by subsequent addition as is the case here.

Since the reaction mechanism contains equilibria before the rate step and since the secondary mechanism can slightly alter the rate constant, no attempt will be made here to discuss the effect of either temperature or ionic strength on the rate of the primary reaction.

The Secondary Reaction.—The first experiments on the secondary mechanism were based on the premise that a fifth-order mechanism (*i.e.*, the primary process) should fall off rapidly in rate as the reaction proceeds and that the secondary mechanism should become the kinetically important process. The reactants were mixed and allowed to stand for 10 to 30 minutes. Aliquots were then taken at measured intervals. The results were not decisive since the amount of catalytic agent varied with time and with each experiment, but runs at different initial concentration gave some information. The rate varied little with changes in the concentration of hydrogen selenite ion and it appeared to be dependent on about the one-half power of the hydrogen ion concentration. Changes in the initial amount of thiosulfate made large differences in the secondary rate; it appeared that the order was between one and two. Addition of inert salt increased the rate to a much larger extent than is the case for the primary reaction, and a plot of the

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(5) J. O. Edwards, *Chem. Revs.*, forthcoming publication.

(6) F. R. Duke, THIS JOURNAL, **70**, 419 (1948).

logarithm of the rate[7] against the square root of ionic strength has a slope of about two.

Four possibilities may be considered for the species which is generated by the primary reaction and which enters the rate law of the secondary reaction. These are tetrathionate ion, selenopentathionate ion, colloidal selenium and elemental selenium dissolved in the water. The first possibility can be eliminated immediately, for the reaction gradually slows down as the selenium precipitates out, whereas the opposite trend would be observed if tetrathionate were the catalyst. It is unlikely that colloidal selenium is the catalyst for the solution in which selenium is coagulating changes from a clear and colorless liquid to a suspension of red macroscopic selenium in five to ten minutes. While this rapid change in constitution is occurring, the reaction rate is decreasing slowly but not to any large extent. Since any reaction involving colloidal selenium would undoubtedly be a heterogeneous reaction, tremendous changes in rate would be expected as the elemental selenium changed from a solution to a precipitate. The amount of selenium which is dissolved in water must be small; we do not think that it is the catalyst, since the rate gradually decreases to a negligible value after the selenium has precipitated out. The most reasonable possibility is the selenopentathionate ion, and further discussion will be based on the assumption that it is the catalyst.

A solution containing a known concentration of selenopentathionate was made up in the following manner: To a beaker containing 10 ml. of 1.03 *N* selenious acid and 0.30 ml. of 36 *N* sulfuric acid and 100 ml. of water was added 100 ml. of 0.102 *N* sodium thiosulfate. After 5 minutes the reaction mixture was diluted to 1 liter in a volumetric flask. Since there was no turbidity, it was assumed that the formation of tetrathionate and selenopentathionate from thiosulfate was quantitative. The concentration of both ions was 2.6×10^{-3} *M* and that of sodium sulfate was 5.2×10^{-3} *M*. The *p*H of the final solution was 3.4 and a negligible amount of selenious acid remained.

In Table IV, data on the kinetics of the secondary reaction are presented; the effects of thiosulfate, hydrogen selenite and selenopentathionate concentrations were investigated. The rate equation which best fits the experimental results is

$$-\mathrm{d}[\mathrm{S_2O_3^{=}}]/\mathrm{d}t = k_3'[\mathrm{S_2O_3^{=}}]^{3/2}[\mathrm{HSeO_3^-}]^{1/2}[\mathrm{Se(S_2O_3)_2^{=}}]^{1/2}$$

where k_3' contains a term in hydrogen ion concentration.

If the approximate value of 1×10^{11} is taken for k_5 at this temperature and ionic strength, it is possible to calculate the contribution that the primary mechanism would make to the over-all rate at this *p*H. The value of *S*, resulting from the primary mechanism alone, which is calculated for the solution in which k_5 would play the most significant part, is 8×10^{-7}. The observed value of *S* for this solution is 10.5×10^{-5}, which is larger by more than two powers of ten. Control experiments when selenopentathionate was absent verified this calculation for the rate was too slow to measure.

TABLE IV

THE KINETICS OF THE SECONDARY MECHANISM

*p*H 5.78 ± 0.04; *t* = 29.95°

A. Dependence on thiosulfate ion concentration

$[\mathrm{HSeO_3^-}] = 3.32 \times 10^{-3}$ *M*; $[\mathrm{Se(S_2O_3)_2^{=}}] = 4.20 \times 10^{-4}$ *M*; [buffer] = 0.140 *M*

$[\mathrm{S_2O_3^{=}}] \times 10^3$ *M*	$S \times 10^5$ [a]	$S \times 10^2/[\mathrm{S_2O_3^{=}}]^{3/2}$	τ [b]
8.22	1.31	1.76	6.5
16.5	3.75	1.76	3.5
32.9	10.5	1.76	...

B. Dependence on hydrogen selenite ion concentration

$[\mathrm{S_2O_3^{=}}] = 1.65 \times 10^{-2}$ *M*; $[\mathrm{Se(S_2O_3)_2^{=}}] = 4.20 \times 10^{-4}$ *M*; [buffer] = 0.140 *M*

$[\mathrm{HSeO_3^-}] \times 10^3$ *M*	$S \times 10^5$ [a]	$S \times 10^4/[\mathrm{HSeO_3^-}]^{1/2}$	τ [b]
1.66	3.00	7.36	3.5
3.32	3.75	6.53	4.0
6.64	6.00	7.36	3.5

C. Dependence on selenopentathionate ion concentration

$[\mathrm{S_2O_3^{=}}] = 1.70 \times 10^{-2}$ *M*; $[\mathrm{HSeO_3^-}] = 6.86 \times 10^{-3}$ *M*; [buffer] = 0.145 *M*

$[\mathrm{Se(S_2O_3)_2^{=}}] \times 10^4$ *M*	$S \times 10^5$ [a]	$S \times 10^3/[\mathrm{Se(S_2O_3)_2^{=}}]^{1/2}$	τ [b]
0.87	3.38	3.62	>25
2.17	4.88	3.31	16
4.34	6.66	3.20	4

[a] *S* is defined in Table I. [b] τ is the time in minutes for the appearance of colloidal selenium.

The order in hydrogen ion concentration was determined by indirect calculations, using experiments in which the concentrations of thiosulfate and hydrogen selenite were equinormal and where selenopentathionate was generated by the primary reaction.

The rate law for the secondary reaction may be written

$$-\mathrm{d}[\mathrm{S_2O_3^{=}}]/\mathrm{d}t = k_3[\mathrm{S_2O_3^{=}}]^2[\mathrm{Se(S_2O_3)_2^{=}}]^{1/2}[\mathrm{H^+}]^n$$

in which the concentrations of reactants are combined in one term and *n* is the order in hydrogen ion concentration. Letting *c* be the initial concentration of thiosulfate and *y* be the amount consumed, the rate equation becomes

$$\mathrm{d}y/\mathrm{d}t = k_3[c - y]^2[y/4]^{1/2}[\mathrm{H^+}]^n$$

The definition

$$k_y = k_3[y/4]^{1/2}[\mathrm{H^+}]^n$$

is made in order that we have the second order equation

$$\mathrm{d}y/\mathrm{d}t = k_y[c - y]^2$$

with which it is possible to solve for k_y from the slope of the second-order plot. Fortunately it was found that k_y was reasonably constant over a fair percentage of the course of the reaction, although this is probably fortuitous and results from the particular conditions of the experiments. Three examples are presented in Fig. 4.

When calculated, the results show conclusively that the order in hydrogen ion concentration (*n*) is one-half. This is in good agreement with the previously estimated value, which came from the study of the effect of change of initial *p*H. In Table

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[7] These experiments were made with equinormal $\mathrm{S_2O_3^{=}}$ and $\mathrm{HSeO_3^-}$, and the data were plotted according to a second-order equation for reasons to be seen later.

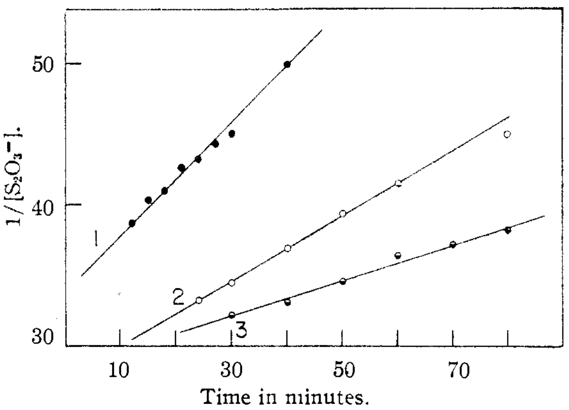

Fig. 4.—Secondary reaction plotted as second order so as to evaluate graphically k_y. Data for same three experiments as Figs. 1 and 2.

V, data for one run are given; these show that the rate is dependent on the one-half order in hydrogen ion concentration during the course of one run. For the three runs of Fig. 4, the average values of k_3 are 2.9×10^4, 3.2×10^4 and 2.8×10^4 liter^2 mole^{-2} min.$^{-1}$; the values of k_y for these experiments are 1.22, 2.32 and 3.95, respectively. The consistency of the values of k_3 shows that the order in hydrogen ion concentration is one-half in separate experiments.

TABLE V

EFFECT OF *p*H ON THE SECONDARY REACTION

t = 29.95°; ionic strength = 0.21; $[S_2O_3^=]$ = $[HSeO_3^-]$ = 3.2×10^{-2} *N*

Time, min.	$[Se(S_2O_3)_2^=] \times 10^3$	*p*H	log k_3[a]
24	2.8	5.14	4.52
30	3.9	5.25	4.50
40	5.8	5.46	4.52
50	7.4	5.70	4.59
60	8.8	5.90	4.65

[a] Calculated from k_y = 2.32; units of k_3 are liter^2 mole^{-2} min.$^{-1}$.

The rate equation for the secondary reaction shows that the mechanism is unquestionably complex. Half-order exponents are often found in free radical reactions and in processes where two intermediates are formed in an equilibrium before the rate step. Further evidence for the complexity of this reaction is found in the constitution of the activated complex $HSeS_5O_9^{-4}$, which appears to have lost one sulfur atom from a thiosulfate ion. Since no mechanism, which is reasonable to our knowledge, can explain the kinetic results, none will be postulated at this time.

Decomposition of Selenopentathionate Ion.—This ion has been observed to be stable in acid solution, and is unstable in alkali; it is also decomposed by excess thiosulfate ion.[2a,4] Experiments to check the rate of decomposition were carried out in conjunction with the kinetic experiments of Table IV. It will be noticed from the data in this table that the rate is markedly dependent on the selenopentathionate concentration, somewhat less dependent on thiosulfate concentration and independent of the concentration of hydrogen selenite. The rapidity of the decomposition in these studies does not allow the determination of an exact rate law, although it appears to be approximately second order in selenopentathionate and first order in thiosulfate.

An interesting phenomenon was observed during the decomposition studies. Two identical solutions were made, each containing 2.1×10^{-3} *M* selenopentathionate at *p*H 1.3. One solution was placed in the sunlight and the second was left in normal laboratory light. Within two hours, practically all of the red selenium had precipitated from the former solution; the latter showed no deposition after ten days. Many other solutions containing this ion had the selenium precipitated out by this photochemical action. These facts suggest the possibility that the secondary reaction is photosensitized, which would be consistent with the observed half-order exponents and a free radical chain mechanism.

The Concentration–Time Curves.—The reaction between selenious acid and thiosulfate ion in the *p*H range from 4 to 6 takes place with two mechanisms and it is complicated by the decomposition of selenopentathionate and the deposition of elemental selenium. As was seen in Figs. 1 and 2, the concentration–time curves and the *p*H–time curves reflect this complexity. If the initial *p*H is 4.5 or greater, the reaction starts slowly and undergoes a marked autocatalysis, whereas below *p*H 4.5 the autocatalysis is not observed. The reason for this is that the primary reaction rate is dependent on the second power of hydrogen ion concentration while the rate of the secondary mechanism is only dependent on the one-half power. For a change in *p*H of 1.00, the rate of the primary reaction varies by a factor of 100 and the rate of the secondary reaction is only altered by a factor of 3.16. When the *p*H is lower than 4.5, the primary rate is faster than the secondary rate.

The secondary reaction, while present, may not cause the curves to appear autocatalytic if the primary reaction uses up 20% of the original concentrations of reactants in rapid fashion. Calculations, assuming constant *p*H, predict that the kinetic effect of the increase in selenopentathionate concentration is overcome by the decrease in rate as the reactants drop in concentration when the reaction has proceeded to only one-fifth of completion. For these reasons, the rate seems to be strictly concentration-dependent when the initial *p*H is about 4.2, while it shows a significant autocatalysis at *p*H 5.0.

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