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

The Rate Law for the Reaction of Selenious Acid and Iodide Ion[1]

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Selenious acid and iodide ion react to form selenium and triiodide ion in acidic solution. The rate of this reaction has been measured over a wide range of concentrations. The rate law for the reaction is $-d(\mathrm{Se^{IV}})/dt = (\mathrm{H_2SeO_3})(\mathrm{H^+})^3(\mathrm{I^-})^4/[k_1(\mathrm{I_3^-}) + k_2(\mathrm{H^+})(\mathrm{I^-})]$, where the values of k_1 and k_2 at 0° and an ionic strength of 0.15 are $5.7_4 \times 10^{-6}$ mole^6 liter^{-6} min. and 1.85×10^{-6} mole^5 liter^{-5} min., respectively. This rate law suggests a mechanism in which two activated complexes, $\mathrm{SeIOH(OH_2)}_n$ and $\mathrm{SeI_3O(OH_2)}_m^-$, exist along a single reaction path. A species of selenium(II) is formed as an intermediate. Measurements have been made as a function of ionic strength and at temperatures between 0 and 25°.

Selenious acid reacts with iodide ion in acidic solution to form selenium and triiodide ion. The equilibrium constant for the reaction

$$\mathrm{H_2SeO_3 + 4H^+ + 4I^- = Se(s) + 2I_2(s) + 3H_2O} \quad (1)$$

has been found to be 6.8×10^{13} at 25°.[2] At concentrations of hydrogen ion and iodide ion of 0.1 M or greater, the reduction of selenious acid by iodide ion is essentially quantitative; use has been made of this in the analysis for selenium(IV).[3] Although the reaction proceeds too rapidly for convenient kinetic studies under the conditions used in the analysis for selenium(IV), it has been possible to study the kinetics at 0° and under concentration conditions which lead to a lower rate. Such conditions (lower hydrogen ion and iodide ion concentrations) not only lower the rate of the forward reaction but also tend to make the rate of the reverse reaction significant. The reaction rates determined in the present study have been measured in the concentration ranges 0.02 to 0.15 M iodide ion, 0.02 to 0.14 M hydrogen ion, 3×10^{-5} to 4×10^{-3} M triiodide ion and 7×10^{-5} to 7×10^{-4} M selenium(IV). The ionic strength was maintained at 0.15 M with sodium perchlorate or sodium chloride. At these concentration conditions, the solutions were not saturated with respect to iodine; the chemical equation for the reaction which was studied is, therefore

$$\mathrm{H_2SeO_3 + 4H^+ + 6I^- = Se(s) + 2I_3^- + 3H_2O} \quad (2)$$

The selenium was formed as a colloidal suspension which slowly precipitated upon standing. Under the most adverse conditions, the reverse reaction rate amounted to 8% of the forward reaction rate at the point at which the rate was measured.[4]

Experimental

The Rate of the Reaction.—The course of the reaction was followed by determining the amount of iodine(0) which had been produced at various times. Aliquots of the reaction mixture were delivered into a phosphate buffer solution giving a final pH value of 4.2–4.6 which contained a slight excess of sodium thiosulfate over that which was required to react with the iodine(0). The excess thiosulfate was then titrated with a standard iodine solution. Under these concentration conditions, no detectable reaction between selenium(IV) and thiosulfate ion[5] or iodide ion occurs over a period of a few hours.

The reactants, hydrogen ion and iodide ion, were present in all of the experiments at a concentration which was relatively high compared to the initial concentration of selenium(IV). During the course of an experiment in which only the reactants, selenium(IV), hydrogen ion and iodide ion, were present initially, the concentrations of selenium(IV) and triiodide ion and the amount of solid selenium changed appreciably. The rate of change of the concentration of selenium(IV) in such an experiment did not conform to any of the simple rate equations which involved the assumption that the rate depended only upon the concentration of the reactants.

Three experiments were performed in order to learn if the colloidal selenium had any effect upon the rate of reaction. In one experiment, the initial concentration of selenium(IV) was 4×10^{-4} M and the concentrations of the other dissolved substances, including triiodide ion, were large compared to it. The initial concentrations in the second experiment were those existing at the midpoint of the first experiment except that no colloidal selenium was present. The initial concentrations in the third experiment were those existing at the midpoint of the second experiment or the three-quarter completion point of the first experiment; again, no colloidal selenium was present. Despite the enormous difference in the amounts of colloidal selenium present in these runs, the rates were the same at the same concentrations of the dissolved species. The rate of this reaction is *not* influenced by the amount of selenium which is present.

A similar series of experiments, in which only the concentration of triiodide ion and the amount of selenium varied, disclosed that the rate of the reaction depended upon the triiodide ion concentration; a retardation resulted as the triiodide ion concentration increased.

It is, nevertheless, possible to establish the rate law for the reaction by comparison of the rates at different concentration conditions. The reaction rate was determined from the slope of the tangent to the smooth curve in a plot of the concentration of selenium(IV) *versus* time. The concentrations existing at the point under consideration were calculated from the known initial composition of the solution, the concentration of iodine(0) which was determined, and the stoichiometry of the reaction.

The Rate Law; Selenium(IV) Dependence.—The dependence of the rate of reaction upon the selenium(IV) concentration has been determined in two series of experiments at relatively high and low concentrations of triiodide ion. The results of these two series of experiments are presented in Fig. 1. The reaction is first order with respect to the concentration of selenium(IV). The points for the series of experiments at the higher concentration of triiodide ion actually conform more closely to an order of 1.1; it is believed that this difference from 1.0 is not of any significance.

Similar series of experiments at low and high triiodide ion concentrations were performed at varying hydrogen ion and iodide ion concentrations. Plots of logarithm (rate) *versus* logarithm (H$^+$) indicated that the order of the reaction with respect to hydrogen ion was 2.0 and 2.7 at 3.3×10^{-5} and

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[1] Taken from a thesis presented by John A. Neptune for the Ph.D. degree, University of Wisconsin, 1952.

[2] H. F. Schott, E. H. Swift and D. M. Yost, THIS JOURNAL, **50**, 721 (1928).

[3] (a) W. Muthman and J. Schafer. *Ber.*, **26**, 1015 (1893); (b) J. H. van der Meulen, *Chem. Weekblad*, **31**, 333 (1934).

[4] In the few experiments in which the reverse rate was significant, the total forward rate may be calculated by

$$\text{total forward rate} = \frac{\text{net forward rate}}{(1 - Q/K)}$$

where K is the equilibrium quotient for reaction 2, which was experimentally determined at 0° to be 4.3×10^{14}, and Q has the same form as K but involves the actual concentrations which exist in the solution under consideration.

[5] C. H. Sorum and J. O. Edwards, THIS JOURNAL, **74**, 2318 (1952).

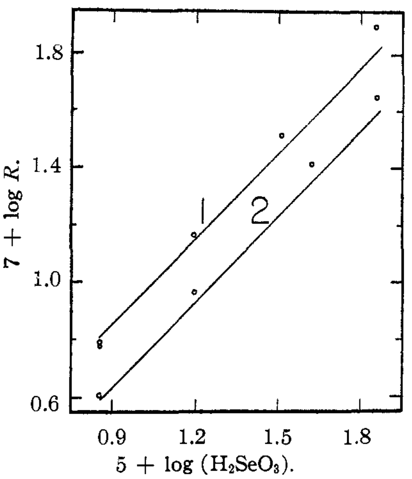

Fig. 1.—The dependence of reaction rate upon the concentration of selenium(IV), (experiments at 0°): curve 1, $(H^+) = 0.0206$ *M*, $(I^-) = 0.060$ *M*, $(I_3^-) = 1.83 \times 10^{-3}$ *M;* ionic strength made up to 0.15 with sodium chloride; curve 2, $(H^+) = 0.0206$ *M*, $(I^-) = 0.030$ *M*, $(I_3^-) = 3.3 \times 10^{-5}$ *M;* ionic strength made up to 0.15 with sodium chloride. (The straight lines correspond to rate equation 6 with the parameters which best fit *all* of the data.)

1.83×10^{-3} *M* triiodide ion, respectively; corresponding plots indicated that the order of the reaction with respect to iodide ion was 3.0 and 3.7 at 3.3×10^{-5} and 1.83×10^{-3} *M* triiodide ion, respectively. The dependence of the reaction rate upon the concentration of these species was more completely elucidated after the manner in which the rate depends upon the triiodide ion concentration had been clarified.

Triiodide Ion Dependence.—As has already been mentioned, the reaction rate was lowered as the concentration of triiodide ion was increased. A series of twenty-six experiments at ten different concentrations of triiodide ion in the range 3.3×10^{-5} to 3.6×10^{-3} *M* have been performed. The results are summarized in Fig. 2, in which the linear relationship between $(\text{rate})^{-1}$ and the concentration of triiodide is shown. Since the reaction has already been shown to be first order in the concentration of selenium(IV), the equation

$$(H_2SeO_3)R^{-1} = k'(I_3^-) + k'' \qquad (3)$$

is valid, where *R* is the reaction rate in moles selenium(IV) per liter per minute, and *k'* and *k''* are "constants" which may depend upon the concentrations of hydrogen ion and iodide ion. This equation involves the concentrations of species H_2SeO_3 and I_3^- rather than the total concentrations of selenium(IV) and iodine(0). The rate constant defined by a rate equation which involves the total concentration of an element in a particular oxidation state will not be constant if different appreciable relative amounts of this element exist as two or more species in the several solutions. Since triiodide ion and non-ionized selenious acid are the dominant forms of iodine(0) and selenium(IV), the rate law is written involving the concentration of these two species; these concentrations may be calculated from the stoichiometric composition of the solution and the appropriate equilibrium quotients.[6,7]

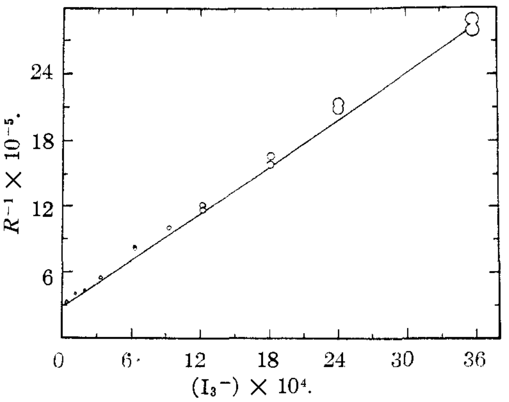

Fig. 2.—The dependence of the reaction rate upon triiodide ion concentration (experiments at 0°). Concentration conditions: $(H^+) = 0.0206$ *M*, $(I^-) = 0.060$ *M*, $(H_2SeO_3) = 7.1 \times 10^{-5}$ *M;* ionic strength made up to 0.15 with sodium chloride. (The straight line is that corresponding to rate equation 6 with the parameters which best fit *all* of the data.)

In the iodide ion concentration range 0.02 to 0.15 *M*, 96.7 to 99.6% of iodine(0) is present as triiodide ion[7]; in the hydrogen ion concentration range 0.02 to 0.14 *M*, 79 to 96% of selenium(IV) is present as selenious acid.[6] This writing of the rate equation in terms of the concentrations of H_2SeO_3 and I_3^-, instead of in terms of the concentrations of $HSeO_3^-$ and I_2, is an arbitrary choice. The complete rate equation would have different hydrogen ion and iodide ion concentration dependences if it were written involving the concentrations of $HSeO_3^-$ and I_2.

Hydrogen Ion and Iodide Ion Dependences.—Data have already been cited which indicate that the dependences of the reaction rate upon the concentrations of hydrogen ion and iodide ion are functions of the concentration of triiodide ion. The problem is the determination of the exponents in the equations

$$k' = k_1(H^+)^a(I^-)^b \qquad (4)$$

and

$$k'' = k_2(H^+)^c(I^-)^d \qquad (5)$$

as well as the numerical values of k_1 and k_2 (*k'* and *k''* are defined by equation 3). A series of experiments in which only the triiodide ion concentration is varied allows a calculation of *k'* and *k''*, the slope and intercept, respectively, in a plot of $(H_2SeO_3)R^{-1}$ *versus* the concentration of triiodide ion. Four such series of experiments were performed in which each series differed from the others only in the concentration of hydrogen ion. The results of these experiments are summarized in the first six columns of Table I. The evaluation of *a* and *c* was carried out by plotting logarithm *k'* and logarithm *k''* *versus* logarithm (H^+); these plots are presented as Fig. 3a. The values of *a* and *c*, so determined, were −3 and −2. The results of four series of experiments in which only the iodide ion concentration varied from series to series are also presented in Table I. The graphical evaluation of *b* and *d*, shown in Fig. 3b, led to the values −4 and −3, respectively.

With the exponents in equations (4) and (5) established, the values of k_1 and k_2 were calculated from the values of *k'* and *k''*. These values are presented in columns 7 and 8 of Table I. The k_1 and k_2 values determined in the series of experiments with varying hydrogen ion concentrations were significantly different from the values determined in the series of experiments with varying iodide ion concentration. This may be due to a subtle medium effect for, although the ionic strength was the same in all experiments, the nature of the electrolyte varied.

The rate law is

$$R = \frac{(H_2SeO_3)(H^+)^3(I^-)^4}{k_1(I_3^-) + k_2(H^+)(I^-)} \qquad (6)$$

where the values of k_1 and k_2 at 0° and an ionic strength of 0.15 are $5.7_4 \times 10^{-6}$ moles^6 liters^{-6} min. and 1.85×10^{-6}

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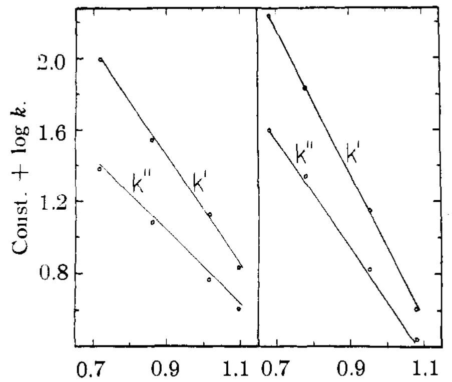
[6] The first ionization constant for selenious acid is 2.4×10^{-3} at 25° (D. M. Yost and H. R. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 331). The equilibrium quotient at 0° and ionic strength 0.15 has been calculated to be 5.4×10^{-3} using the relationship developed by Pitzer (THIS JOURNAL, **59**, 2365 (1937)) to make the correction for the change of temperature. In making the correction for the change of ionic strength, it was assumed the activity coefficient of un-ionized selenious acid does not deviate significantly from unity and that the mean activity coefficient of hydrogen ion and hydrogen-selenite ion varies with ionic strength in the same manner as the mean activity coefficient of hydrochloric acid, a behavior which is observed for some other weak acids (H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publ. Corp., New York, N. Y., 1950, p. 575).

[7] M. Davies and E. Gwynne, THIS JOURNAL, **74**, 2748 (1952).



(a) 2 + log (H⁺). (b) 2 + log (I⁻).

Fig. 3.—The dependence of k' and k'' upon (a) hydrogen ion concentration and (b) iodide ion concentration. (The lines in (a) have slopes −3 and −2; in (b), the slopes are -4 and -3. The positions of the lines are those calculated using the values $5.7_4 \times 10^{-6}$ moles^6 liters^{-6} min., and 1.85×10^{-6} moles^5 liters^{-5} min. for k_1 and k_2, respectively.)

moles^5 liters^{-5} min., respectively. This rate equation with these numerical values of k_1 and k_2 has been used to calculate the value of R for the 103 experiments which were performed in the course of this work. The average deviation between the calculated and observed values of R is 6%. Since the concentration range, which has already been mentioned, is a large one, it is felt that this degree of agreement is good.

TABLE I

A SUMMARY OF EXPERIMENTS WHICH ESTABLISHES THE ORDER OF THE REACTION WITH RESPECT TO THE CONCENTRATIONS OF HYDROGEN ION AND IODIDE ION. THE VALUES OF k_1 AND k_2

Concn., mole/l. (H⁺)	(I⁻)	No. of experiments in series	$k' \times 10^{-4}$	k''	Av. % dev.[a]	$k_1 \times 10^6$	$k_2 \times 10^6$
0.0206	0.048	5	12.9	39.8	2.6	5.98	1.86
.0206	.060	26	5.14	21.8	2.4	5.82	1.99
.0206	.090	6	1.07	6.60	2.8	6.15	2.03
.0206	.120	5	0.307	2.76	1.2	5.57	2.02
.0518	.030	6	4.92	24.0	1.7	5.54	1.74
.0726	.030	6	1.76	12.2	1.7	5.46	1.74
.1038	.030	5	0.668	5.80	1.3	6.04	1.69
.1246	.030	5	0.341	4.03	2.5	5.35	1.69

[a] The average per cent. deviation for a particular series refers to the difference between the observed values of the rate and those calculated using equation 3 with the tabulated values of k' and k'' for that series.

It is now clear why the experiments mentioned in the section on selenium(IV) dependence at high and low concentrations of triiodide ion yielded different orders for hydrogen ion and iodide ion; furthermore, the reason for the nonintegral values of the order at high concentrations of triiodide ion is apparent. In the experiments which have already been mentioned, the low concentration of triiodide, 3.3×10^{-5} M, was sufficiently low that the term $k_2(H^+)(I^-)$ in the denominator was dominant. At the high concentration of triiodide, 1.83×10^{-3} M, the term $k_2(H^+)(I^-)$ still contributes about 26% of the magnitude of the denominator in the middle of the hydrogen ion and iodide ion concentration ranges.

The Kinetic Salt Effect.—The dependence of the rate of reaction upon the ionic strength has been determined under various concentration conditions. Two series of experiments were performed in which each of the two terms in the denominator of the rate law was made important. The data from these experiments are presented in Fig. 4. If the values of k_1 and k_2 which were established at an ionic strength of 0.15 are used, it is calculated that the term $k_1(I_3^-)$ is 75% of the denominator for the upper pair of curves, while the term $k_2(H^+)(I^-)$ is 95% of the denominator for the lower pair of curves. The ionic strength range is too high for any quantitative correlation with the Brönsted–Debye and Hückel equation. It might be expected, however, that the difference in the charge type of the two reactions leading to the two activated complexes would lead to discernible differences in the electrolyte effect. Such is the case, for the values of d log $R/\mathrm{d}\sqrt{u}$ at low ionic strength are greater if $k_1(I_3^-)$ is important. The scales of Fig. 4 have been chosen such that both sets of curves would have the same slope at zero ionic strength if the Brönsted–Debye and Hückel limiting equation were obeyed and if, for each set of curves, one of the terms in the denominator of the rate law were dominant.

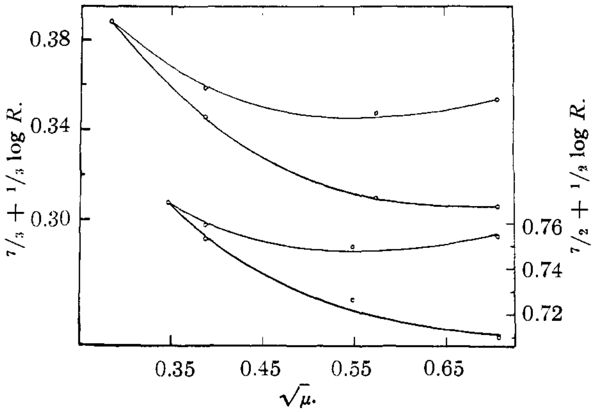


Fig. 4.—The dependence of the rate of reaction upon the ionic strength. (Note that the abscissa scale does not extend to zero on the left-hand side.) In each pair of curves, the upper curve refers to experiments in which the electrolyte in excess of the reactants is sodium chloride while the lower curve refers to experiments involving sodium perchlorate. Reactant concentrations: upper curves (ordinate on left), $(H^+) = 0.031$ M, $(I^-) = 0.048$ M, $(I_3^-) = 1.23 \times 10^{-3}$ M; lower curves (ordinate on right), $(H^+) = 0.1038$ M, $(I^-) = 0.018$ M, $(I_3^-) = 3.3 \times 10^{-5}$ M.

The Temperature Coefficient of the Rate.—The dependence of the rate upon temperature was determined over a 25° temperature range. In a series of runs at concentration conditions: $(\mathrm{Se^{IV}})_{\mathrm{initial}} = 1.07 \times 10^{-4}$ M, $(H^+) = 0.0206$ M, $(I^-) = 0.030$ M, and $(I_3^-) = 3.3 \times 10^{-5}$ M, the values of $R \times 10^7$ were 4.04, 5.59 and 8.9 moles liter^{-1} min.$^{-1}$ at 0, 10 and 25°, respectively. These data lead to an apparent activation energy of 5200 cal. Another series of experiments were carried out under the same concentration conditions except for the concentrations of iodide ion and triiodide ion which were 0.090 M and 1.83×10^{-3} M, respectively. The values observed for $R \times 10^7$ were 26.2, 31.6 and 40.6 at 0, 10 and 25°, respectively. These data lead to an apparent activation energy of 3000 cal. At the concentration conditions of the first mentioned series of experiments, the values of k_1 and k_2 obtained at 0° lead to the conclusion that the term $k_2(H^+)(I^-)$ is 86% of the denominator of the rate law. Under the other set of concentration conditions, the term $k_1(I_3^-)$ accounts for 75% of the magnitude of the denominator of the rate law. Therefore, these values of the apparent activation energy cannot be associated exclusively with either k_1 or k_2.

Experimental Details.—The graphical method of obtaining the rate is not highly precise; it is estimated that the slope determination may introduce an uncertainty of about 3% in the rates. This uncertainty, combined with slight uncertainties in time and concentrations suggest an uncertainty of about 5% in the rates.

In all figures the diameter of the circles corresponds to 5% in the magnitude of the quantity plotted as the ordinate.

For most experiments, the temperature was 0.0 ± 0.1°; the thermostat bath was an ice–water mixture.

Samples were taken with a 100-ml. pipet with a drainage time of 13 seconds. The time of sampling was taken when one-half the sample was delivered. The reaction mixtures with the highest rates had half-periods of 3 to 4 minutes, while those with the lowest rates had half-periods of several hours. The maximum uncertainty in the time measurements was considered to be 2 seconds; except for the fastest reactions, the error introduced by this uncertainty is negligible.

Reagent grade chemicals were used without further purification, with the exception of selenious acid, sodium selenite and sodium perchlorate, which were Fisher C.P. Grade. These were recrystallized from water. The water used for all solutions was doubly distilled, the second distillation being from alkaline permanganate in all-Pyrex apparatus. The selenium(IV) solutions were standardized by the method of van der Meulen[3b]; the sodium perchlorate solutions by the method suggested by Walton[8]; and the other solutions by the usual volumetric methods.

No differences in reaction rates were observed when duplicate runs were performed using chemicals from different sources, indicating that no trace impurity in any reagent was acting as a catalyst. Duplicate runs were also made using solutions saturated with oxygen and solutions through which nitrogen was bubbled for 30 minutes. Since no significant difference was found in the rates, no attempt was made to exclude atmospheric oxygen from the reaction mixtures. At the concentrations used, air oxidation of iodide was not important. Precautions were taken to keep all reaction mixtures out of direct sunlight.

For the determination of the equilibrium quotient for reaction 2, solutions of selenium(IV), perchloric acid, iodide ion and triiodide ion were stored in stoppered containers at 0.0°. The reaction was allowed to continue until the triiodide concentration approached a constant value. The equilibrium concentrations for the other reactants were calculated from the original concentrations and the stoichiometry of the reaction. A blank solution containing the approximate equilibrium concentrations, except that it contained no selenium(IV), permitted correcting for air oxidation of iodide or volatilization of iodine.

Discussion

The form of the rate equation for a chemical reaction gives the composition of the activated complex for the reaction. Two different activated complexes are important for this reaction, depending upon the relative magnitude of $k_1(I_3^-)$ and $k_2(H^+)(I^-)$. They have the compositions $SeI_3O(OH_2)_m$, and $SeIOH(OH_2)_n$. (Since the order of the reaction with respect to the solvent is not known, the numbers of water molecules in the activated complexes are not known.) The manner in which the dependence of the reaction rate upon the triiodide ion concentration varies (*i.e.*, a decrease in the order with respect to the triiodide ion concentration with an increase in the concentration of triiodide ion) indicates that the mechanism is *not* one involving two different independent reaction paths. A reaction scheme which satisfies the rate law is

$$H_2SeO_3 + 2H^+ + 3I^- + (m-2)H_2O = \{SeI_3O(OH_2)_m{}^-\} = SeO(OH_2)_a + I_3^- + (m-a)H_2O \quad (7)$$

$$SeO(OH_2)_a + H^+ + I^- + (n-a)H_2O = \{SeIOH(OH_2)_n\} = \text{products or substances which rapidly yield products} \quad (8)$$

The activated complexes, enclosed in brackets in equations 7 and 8, do have the compositions demanded by the rate law. The unstable intermediate, the existence of which is indicated by the rate law, is $SeO(OH_2)_a$, a species of selenium(II). There is a competition for this intermediate; it may be oxidized by triiodide ion to give the original reactants or it may be reduced in a reaction with hydrogen ion and iodide ion. If $k_1(I_3^-) \gg k_2(H^+)(I^-)$, the concentration of this intermediate will attain the value corresponding to the establishment of equilibrium in reaction 7. Under such concentration conditions, reaction 8 would be spoken of as the rate-determining reaction and $SeIOH(OH_2)_n$ would be the activated complex for the reaction. If $k_2(H^+)(I^-) \gg k_1(I_3^-)$, the selenium (II) species is consumed in reaction 8 so rapidly that it does not attain the concentration corresponding to equilibrium in reaction 7. Under these conditions reaction 7 would be spoken of as rate-determining, and $SeI_3O(OH_2)_m$ would be the activated complex for the reaction.

Reaction equations 7 and 8 give a *minimum* amount of information regarding the intimate mechanism, but they give the *maximum* amount of information which can be obtained from these kinetic data. *Any mechanism* having two possible activated complexes along a single reaction path which have the compositions mentioned is consistent with the rate data. The reaction undoubtedly occurs in several steps, possibly of the type suggested by Edwards[9]; these rate data alone, however, allow no more to be said regarding the reaction mechanism.

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(8) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 173.

(9) J. Edwards, *Chem. Revs.*, **50**, 455 (1952).