Kinetics of the Reduction of Selenious Acid by Sulfur Dioxide. II. Reduction in Acidic Solution with Sulfuric Acid[*]

By Keinosuke HAMADA

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This paper deals with the kinetics of the reduction of selenious acid in sulfuric acid by sulfur dioxide. Amelin and Yashke$^{1)}$ investigated the reduction of selenious acid in concentrated sulfuric acid (60~80% by weight), and reported that the reaction was of first order with respect to selenious acid and to sulfur dioxide. The present author has studied the reduction of selenious acid by sulfur dioxide in dilute sulfuric acid, and has obtained different results from that obtained when concentrated sulfuric acid is utilized. The same method as that described in Part I$^{2)}$ of this series was used. However, since it was found that the reaction in sulfuric acid was reversible, the method of measurements was improved by taking account of the equilibrium in the reversible reaction. The influences of temperature, initial concentration of selenious acid and hydrogen ion concentration on the reaction were investigated, and also general equations were derived for k_2[*1] and k_2' which were rate constants of the forward and reverse reactions.

Experimental

Materials. — 0.736, 0.368 and 0.184 mol./l. aqueous solutions of selenious acid were prepared by dissolving extra pure reagent selenious acid in distilled water. Also prepared were 6.0, 4.5, 3.0 and 1.5% (by volume) sulfuric acid by diluting the first grade reagent sulfuric acid (s. g. about 1.84) with distilled water. pH[*2] values were 0.08, 0.22, 0.38 and 0.62, and their hydrogen ion concentrations were evaluated to be 0.83, 0.60, 0.42 and 0.24 g. ion/l., respectively. The liquid sulfur dioxide was purchased.

Measurements. — This experiment was performed by means of the same procedures as those reported in Part I$^{2)}$ of this series except that sulfuric acid was used in place of hydrochloric acid. However, since it was discovered that the reaction in sulfuric acid was reversible, the procedure suitable to this factor was adopted. That is, after the expected time for the reaction had elapsed, the precipitated selenium was filtered with a glass filter (1G-4)[*3]. Then the selenium was washed with dilute hydrochloric acid and water. Hereafter, the experimental procedures are the same as those in Part I$^{2)}$ of this series.

Results and Discussion

Selenious Acid Concentration Dependence of the Reduction of Selenious Acid. — Ten milliliters of the three selenious acid solutions were diluted to 200 ml. with 4.5% (by volume) sulfuric acid ($[H^+]=0.60$), the concentrations of the experimental solutions of selenious acid being 0.0092, 0.0184 and 0.0368 mol./l., respectively. These solutions were reduced by sulfur dioxide at constant temperature (60°C). Weights of precipitated selenium were converted into percentage completion, and the plot of the percentage completion against elapsed time (sec.) is shown in Fig. 1.

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[*] Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) A. G. Amelin and E. V. Yashke, *Proc. Acad. Sci. U. S. S. R. Sec. Chem.*, **108**, 313 (1956); *Chem. Abstr.*, **51**, 54g (1957); *Chem. Zentr.*, **128**, 6688 (1957).

2) Part I: This Bulletin, **34**, 593 (1961).

[*1] k_2 does not mean the rate constant of the second order reaction, but the rate constant of reaction in sulfuric acid.

[*2] Measured by a pH-meter with 0.01 pH accuracy.

[*3] Since the present reaction is reversible, diluting reactants with water can not be adopted to stop the process of the reaction. The effects of a reverse reaction appear conspicuously.

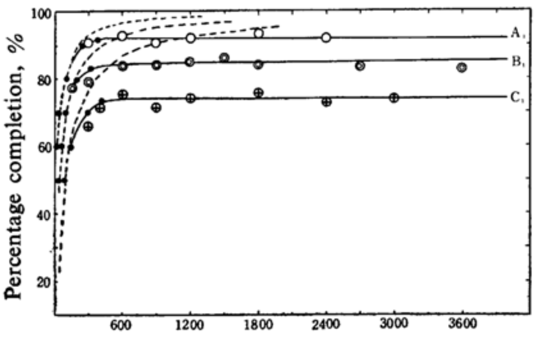

Fig. 1. H_2SeO_3 concn. dependence of the reduction of H_2SeO_3 at const. temp. (60°C) and const. [H^+] (0.60 g. ion/l.).
○ 0.0368 mol./l. ◎ 0.0184 mol./l.
⊕ 0.0092 mol./l. • calculated by Eq. 4.
Dotted lines: forward reaction with rate constant obtained from Eq. 1, when reverse reaction does not occur.

Each curve of Fig. 1 reaches an equilibrium, which is very different from the results in hydrochloric acid[2]. It is certain that the present reaction which comes to equilibrium is reversible[3].

The lines estimated from the experiment in the region below 60% completion of reaction are in good accordance with those obtained from Eqs. 1 and 2 based on only the forward reaction[2] (dotted lines).

Accordingly, the effect of the reverse reaction can be neglected in the region below 60% completion, where the reaction appears to be similar to the simple reaction in hydrochloric acid.

Provided that the reaction in sulfuric acid is of the second order with respect to selenious acid as it was in the case of hydrochloric acid, the rate constant k_2 for the forward reaction can be calculated by $t_{1/2}=1/(k_2a)$*4.

In the region below 60% completion, the author could not obtain any experimental data which could discriminate between curves A_1, B_1 and C_1. However, the value of k_2 in the reaction for curve C_1 is calculated to be 1.278 l. mol^{-1} sec^{-1} from $t_{1/2}=1/(k_2a)$, since the half time ($t_{1/2}$) is evaluated to be 85 sec. from the curve C_1 of Fig. 1, which is estimated from the experiment ($a=0.0092$ mol./l.).

The general equation for the rate constant of the reaction in hydrochloric acid was obtained as follows[2];

$$k_1=2.054\times10^{15}\times[H^+]^2\times\exp(-E/\boldsymbol{RT})$$
$$(E=24.5\ \text{kcal./mol.})$$

When the experimental conditions for curve C_1, 60°C and 0.60 g. ion/l., are substituted for T and [H^+] in the above equation, the rate constant can be calculated to be 0.0629 l. mol^{-1} sec^{-1}. This value is far below the above-mentioned value (1.278 l. mol^{-1} sec^{-1}), so it has to be multiplied by 20 in order to be in good accordance with the latter value. In this way, the general equation for rate constant k_2 of the forward reaction in sulfuric acid is expressed tentatively as follows:

$$k_2=20\times k_1$$
$$k_2=4.108\times10^{16}\times[H^+]\times\exp(-E/\boldsymbol{RT})$$
$$(E=24.5\ \text{kcal./mol.}) \qquad (1)$$

The values of k_2 estimated from the experiment in the reaction for curves A_1 and B_1 of Fig. 1 are in accordance with the ones calculated from Eq. 1.

The reverse rate constant k_2' can be obtained by substituting the value of forward rate constant k_2, which is calculated from Eq. 1 in Eq. 3. When k_2 and k_2' are substituted in Eq. 4, the parts of the curves in Fig. 1 are drawn theoretically. The curvatures obtained from the experiment are in good accordance with those drawn by the calculated values from Eq. 4.

From these facts it is concluded that the values of k_2 based on Eq. 1 are correct.

Eq. 1 is derived by assuming that the activation energy E of the reaction in sulfuric acid is equal to the one in hydrochloric acid ($E=24.5$ kcal./mol.). However, the coefficient of 20 may be due to the difference of the activation energy in each case. Although the energy of activation could not be obtained experimentally, it will be possible for it to be obtained by calculation. The values of k_2 at 60, 50, 40 and 30°C are calculated with Eq. 1 to be 1.258, 0.400, 0.118 and 0.032 l. mol^{-1} sec^{-1}, respectively. The line A of Fig. 3 shows the plotting of the logarithm of k_2 against the reciprocal of the absolute temperature. Each point falls upon a straight line. It follows from the slope of the straight line that the energy of activation is 22.5 kcal./mol. So, Eq. 1 is rewritten as follows:

$$k_2=2.054\times10^{15}\times[H^+]^2\times\exp(-E/\boldsymbol{RT})$$
$$(E=22.5\ \text{kcal./mol.}) \qquad (1')\text{*5}$$

The dotted lines in each figure are obtained from Eqs. 1 and 2,

$$t=p/\{k_2a(a-p)\}=x/\{k_2a(1-x)\}$$
$$(p=ax) \qquad (2)\text{*6}$$

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3) S. Glasstone, "Elements of Physical Chemistry", Maruzen, Tokyo (1958), p. 600.

*4 Eq. 3 in Part I[2] of this series (as $n=2$).

*5 Eq. 1′ is the same equation as Eq. 1. But, for the general equation of rate constant, the expression of Eq. 1′ seems to be better than the one of Eq. 1.

*6 Eq. 2 in Part I[2] of this series (as $n=2$).

where t is the elapsed time (sec.) of reaction, p the reduced quantity of selenious acid (mol./l.) when time t has elapsed, x percentage completion (%) when time t has elapsed, k_2 rate constant (l. mol^{-1} sec^{-1}), and a initial concentration of selenious acid (mol./l.).

The reversible reaction which is of the second order with respect to selenious acid can be expressed mathematically[3] by

$$-\mathrm{d}(a-p)/\mathrm{d}t=\mathrm{d}p/\mathrm{d}t=k_2(a-p)^2-k_2'p^2 \tag{3}$$

[4]*7

The solution of Eq. 3 is as follows, ($p=ax$)

$$t=\frac{2.303}{2a\sqrt{k_2k_2'}}\times\log \left|\frac{\{(k_2-k_2')x-k_2-\sqrt{k_2k_2'}\}/(k_2-k_2')x-k_2+\sqrt{k_2k_2'}}{(-\sqrt{k_2k_2'}-k_2)/(\sqrt{k_2k_2'}-k_2)}\right| \tag{4}$$

The curvatures of the practical lines are drawn according to Eq. 4. Values of k_2' in Eq. 4 can be obtained from Eq. 5.

As the reverse reaction occurs, selenium must be dissolved in dilute sulfuric acid. However, the purchased selenium is not dissolved in dilute sulfuric acid or in basic solution (NH_4OH)*8. This is inconsistent with the fact that the reduction of selenious acid in dilute sulfuric acid is a reversible reaction. This discrepancy can be solved by assuming that α selenium is dissolved in dilute sulfuric acid or in a basic solution, whereas β selenium is not dissolved*8. The purchased selenium is dried at 100∼105°C, and is of the β form.

On the contrary, the selenium produced by reducing selenious acid below 99°C is of the α form, because the allotropic transition temperature of selenium from α to β is 99°C[5].

At equilibrium of the reversible reaction, it is evident that $\mathrm{d}p_\mathrm{m}/\mathrm{d}t=0$ in Eq. 3 where p_m is the value of p at equilibrium (the value of p at equilibrium is equal to the maximum value of p). When p is equal to $p_\mathrm{m}(ax=ax_\mathrm{m})$, Eq. 5 can be derived from Eq. 3 as follows,

$$\begin{aligned}\mathrm{d}p/\mathrm{d}t&=k_2(a-p_\mathrm{m})^2-k_2'p^2{}_\mathrm{m}\\&=k_2a^2(1-x_\mathrm{m})^2-k_2'a^2x_\mathrm{m}{}^2=0\end{aligned} \tag{5}$$

where x_m is the maximum percentage completion at equilibrium. The values of x_m obtained from Fig. 1 are 92, 85 and 74%, respectively. When the values of x_m and k_2 (1.258 l. mol^{-1} sec^{-1}) obtained from Eq. 1 are substituted in Eq. 5, then the values of k_2' can be calculated to be 0.009, 0.039 and 0.155 l. mol^{-1} sec^{-1} for curves A_1, B_1 and C_1 in Fig. 1.

Table I shows the relation between the initial concentration of selenious acid, a, and the reverse rate constant, k_2'.

It is evident from Table I that k_2' is inversely proportional to a^2.

TABLE I. RELATION BETWEEN a^2 AND k_2'

a, mol./l.	x_m, %	k_2	k_2'	$a^2k^{2'}\times10^{-5}$
0.0368	92	1.258	0.009	1.30
0.0184	85	1.258	0.039	1.33
0.0092	74	1.258	0.155	1.24

Temperature Dependence of the Reduction of Selenious Acid. — At constant initial concentration of selenious acid (0.0184 mol./l.) and hydrogen ion concentration (0.60 g. ion/l), selenious acid in sulfuric acid is reduced by sulfur dioxide at different temperatures, 60, 50, 40 and 30°C.

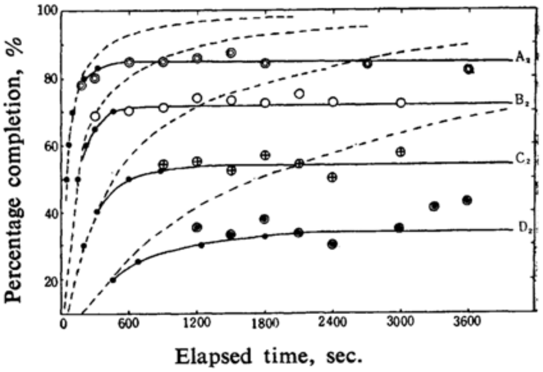

Fig. 2. Temp. dependence of the reduction of H_2SeO_3 at const. [H_2SeO_3] (0.0184 mol./l.) and const. [H^+] (0.60 g. ion/l.).
◎ 60°C ○ 50°C ⊕ 40°C ⊙ 30°C
• Calculated by Eq. 4.
Dotted lines: Ref. 2, Fig. 1

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[4] A. Wattilon and F. Grunderbeck, *Bull. soc. chim. Belges*, **65**, 657 (1956); *Chem. Abstr.*, **51**, 7103 (1957).

*7 Although the precipitated selenium coagulates gradually at a temperature above about 40°C in this experiment, the size of selenium particles prepared at the outset of the reaction is ultramicroscopic or electronmicroscopic. The very fine particles of selenium are dispersed by the passage of sulfur dioxide at the onset of the reaction. The reaction in the reverse direction is one where the dissolving of the precipitated selenium on its surface takes place. When k_8 is a rate constant for dissolving the solid and S is the constant dependent on the surface of the solid, k_8Sp^2 expresses a rate of the reverse reaction. If S is constant under the present experimental conditions, k_8Sp^2 can be expressed by $k_2'p^2$ in Eq. 3. From Figs. 1, 2 and 4, it is seen that the higher the temperature, greater hydrogen ion concentration and initial concentration of selenious acid are, the better are the experimental data in accordance with Eq. 3. If S is variable under all experimental conditions, Eq. 3 can not be derived.

*8 Eq. 6 shows that the lower the hydrogen ion concentration, the higher is the value of k'_2 (rate constant of reverse reaction), i.e., selenium is dissolved in basic solution more easily than in acidic solution. In fact, selenium produced by reducing selenious acid at 60°C disappears by adding basic solution (NH_4OH), but selenium dried over 100°C does not dissolve in basic solution.

[5] Roger Dolique et al., *Bull. soc. chim. France, Mém.* [5], **10**, 231 (1943); *Chem. Abstr.*, **38**, 6156–8 (1944).

The results are shown in Fig. 2, where the precipitated selenium is converted into percentage completion. The values of k_2 at 60, 50, 40 and 30°C are calculated with Eq. 1 to be 1.258, 0.400, 0.118 and 0.032 l. mol^{-1} sec^{-1}, respectively. The values of x_m at the above temperature can be obtained from Fig. 2, and they are 85, 72, 54 and 34%, respectively. Making these substitutions for k_2 and x_m in Eq. 5, the values of k_2' at each temperature can be calculated to be 0.039, 0.060, 0.086 and 0.121 l. mol^{-1} sec^{-1}.

Line B of Fig. 3 shows the plotting of the logarithm of k_2' against the reciprocal of the absolute temperature ($1/T$). It is evident that experimental points fall upon a straight line. The relation between the rate constant of reverse direction and the temperature can be derived from the straight line B in Fig. 3 as follows.

$$k_2' \propto \exp(-E/\boldsymbol{R}T)$$

The energy of activation E can be calculated to be −8.06 kcal./mol. from the slope of the line **B** in Fig. 3.

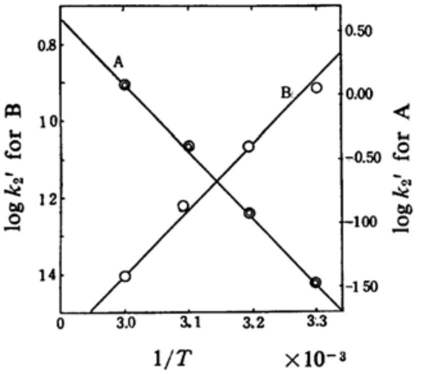

Fig. 3. Arrhenius' plot of the forward and reverse reaction.

Hydrogen Ion Concentration Dependence of the Reduction of Selenious Acid. — At constant initial concentration of selenious acid (0.0184 mol./l.), constant temperature (60°C) and various hydrogen ion concentrations (0.83, 0.60 and 0.042 g. ion/l.), selenious acid in sulfuric acid was reduced by sulfur dioxide.

The results are shown in Fig. 4, where precipitated selenium is converted into a percentage completion. The values of k_2 and k_2' can be calculated from Eqs. 1 and 5, (see Table II).

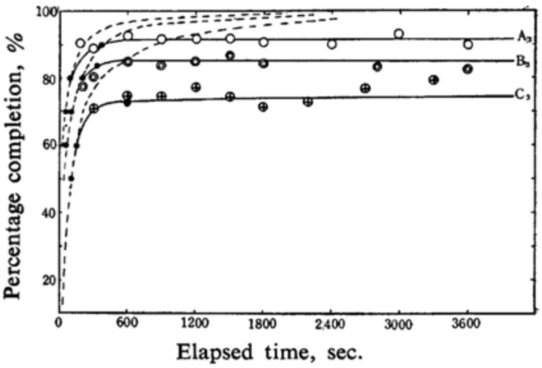

Fig. 4. [H$^+$] dependence of the reduction of H_2SeO_3 at const. [H_2SeO_3] (0.0184 mol./l.) and const. temp. (60°C).

○ 0.83 g. ion/l. ◎ 0.60 g. ion/l.
⊕ 0.42 g. ion/l. • Calculated by Eq. 4.
Dotted lines: Ref. Fig. 1

TABLE II. RELATION BETWEEN k_2' AND [H$^+$]

[H$^+$]	k_2	x_m, %	k_2'	[H$^+$]^2	$k_2' \times$ [H$^+$]^2 ($\times 10^{-3}$)
0.83	2.408	91.5	0.021	0.689	14.33
0.60	1.258	85.0	0.039	0.369	14.04
0.42	0.617	74.0	0.076	0.176	13.37

From Table II, the rate constant of reverse direction, k_2', is inversely proportional to the square of hydrogen ion concentration, [H$^+$]^2. According to the above-mentioned selenious acid concentration, temperature and hydrogen ion concentration dependence of the reverse reaction, the general equation for the reverse rate constant k_2' can be derived as follows:

$$k_2' = 2.413 \times 10^{-11} \times \{1/(a^2[\mathrm{H}^+]^2)\} \times \exp(-E/\boldsymbol{R}T) \qquad (6)$$

where a is the initial concentration of selenious acid, [H$^+$] hydrogen ion concentration, E activation energy (-8.06×10^3 kcal./mol.), $\boldsymbol{R}$ the gas constant and T the absolute temperature.

Also, the data of curve B_1 in Fig. 1, curve A_2 in Fig. 2 and curve B_3 in Fig. 3 are adopted for the above Eq. 6.

Relation among Rate Constant, Maximum Percentage Completion and Initial Concentration of Selenious Acid.—Fig. 5 shows the plotting maximum percentage completion x_m against

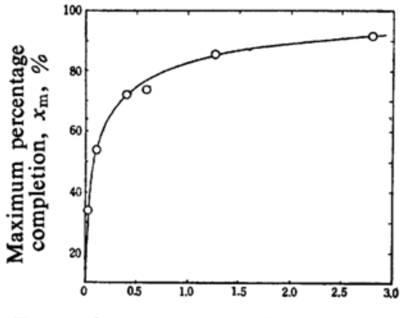

Fig. 5. Plot of maximum percentage (x_m) against forward rate constant (k_2).

forward rate constant k_2 at the constant initial concentration of selenious acid (0.0184 mol./l.). The experimental equation which expresses the relation between x_{m} and k_2 can be derived from Fig. 5 by

$$x_{\mathrm{m}}=0.828\times k_2{}^{0.114} \quad (\text{at } a=0.0184\ \text{mol./l.}) \qquad (7)$$

When the consideration of initial concentration of selenious acid a is taken into Eq. 7, the relationship between k_2, x_{m} and a can derived as follows,

$$x_{\mathrm{m}}=1.306\times(k_2\cdot a)^{0.114} \qquad (8)$$

Summary

(1) The reduction of selenious acid in sulfuric acid by sulfur dioxide is a reversible reaction, because the reaction has an equilibrium and the process of the reaction is in good accordance with the equation which expressed mathematically the reversible reaction, that is,

$$-\mathrm{d}(a-p)/\mathrm{d}t=\mathrm{d}p/\mathrm{d}t=k_2(a-p)^2-k_2'p^2$$

(2) Up to the present time the rate constant k_2 of the forward reaction was derived by substitution of the experimental data for x_{m} in the following equation,

$$k_2=\{2.303x_{\mathrm{m}}/2a(x_{\mathrm{m}}-1)t\}$$
$$\times\log[(x-x_{\mathrm{m}})/\{(2x_{\mathrm{m}}-1)x-x_{\mathrm{m}}\}]$$

The general equation for k_2, which does not depend on x_{m}, has been obtained as follows,

$$k_2=2.054\times10^{15}\times[\mathrm{H}^+]^2\times\exp(-E/\boldsymbol{RT})$$
$$(E=22.5\ \text{kcal./mol.})$$

The rate constant k_2' of the reverse reaction can be calculated by

$$k_2'=2.413\times10^{-11}\times\{1/(a^2[\mathrm{H}^+]^2)\}$$
$$\times\exp(-E/\boldsymbol{RT}) \quad (E=-8.06\ \text{kcal./mol.})$$

(3) It has not previously been reported that α selenium is dissolved in dilute sulfuric acid (below 85% by weight), as shown by the present experimental procedure.

(4) The results obtained from this study are useful in the recovery and refinining of selenium. Then application to the recovery and refining of selenium will be expressed in another succeeding paper.

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Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima