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

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Raw materials for the production of selenium depend heavily on a sludge and a copper slime, which are obtained as a by-product of a sulfuric acid factory and a copper refinery, respectively. In order to investigate the behavior of selenium at the sulfuric acid production plant, to increase the yield of selenium recoverable from the sulfuric acid plant source and to establish a simple method for the refining of these raw materials, the following series of studies were undertaken.

Consideration will be given first to the kinetics of the reduction of selenious acid in hydrochloric acid by sulfur dioxide. The percentage completion of these reactions is calculated by weighing the selenium precipitated from a solution. Sulfur dioxide is passed into a solution continuously, so that the reaction is of zero order with respect to sulfur dioxide.

It has been proved that the reduction of selenious acid was of the second order with respect to selenious acid. Furthermore, a general equation was derived for the rate constant of the reaction by studying the effects of hydrogen ion concentration and temperature upon it.

Experimental

Materials.—1.752, 0.736, 0.368 and 0.172 mol./l. aqueous solution of selenious acid were prepared by dissolving extra pure reagent selenious acid in distilled water. On the other hand, 12, 6, 4.5 and 3% (by volume) hydrochloric acid solutions were prepared by diluting the first grade reagent hydrochloric acid (s. g. 1.18~1.19) with distilled water. The pH[*1] values of these acid solutions were 0.02, 0.31, 0.42 and 0.59, which corresponded to 0.96, 0.49, 0.38 and 0.26 g. ion/l. of hydrogen ion concentration[*2], respectively. Liquid sulfur dioxide was purchased from Befu Chemical Industrial Co.

Measurements.—Experimental solutions were prepared as follows. Ten milliliters of the above aqueous solutions of selenious acid were placed in a 200 ml. measuring flask, which was filled with the above-mentioned dilute hydrochloric acid. The solution was poured into a 300 ml. Erlenmeyer's flask, and kept at a constant temperature within ±0.1°C by a thermostat, and then sulfur dioxide was passed into the solution. The sulfur dioxide was initially passed through a washing bottle filled with water kept at the same constant temperature. Each of the selenious acid solutions was reduced by sulfur dioxide in four kinds of hydrochloric acid solutions at various temperatures.

After a certain period, the contents in an Erlenmeyer's flask was poured into 600 ml. of distilled water. In this way the reaction could be prevented owing to the decrease of the hydrogen ion concentration as well as temperature[1]. Precipitated selenium was filtered with a previously weighed glass filter (1G-4), washed by water, dried at 105~110°C in an air bath and then weighed.

Percentage completion of reaction is expressed with (precipitated selenium/initial selenium in the solution) × 100.

Results and Discussion

Selenious Acid Concentration Dependence of the Reduction of Selenious Acid.—Concentrations of the prepared selenious acid solutions in hydrochloric acid were 0.0876, 0.0368, 0.0184 and 0.0086 mol./l., respectively. At constant temperature (70°C) and constant hydrogen ion concentration (0.49 g. ion/l.), these selenious acid solutions were reduced by sulfur dioxide. The weight of precipitated selenium was converted into percentage completion according to the above expression. Fig. 1 shows the selenious acid concentration dependence of the reduction of selenious acid by plotting the percentage completion against the elapsed time.

The values of half time ($t_{1/2}$) can be obtained from Fig. 1, and these are 100, 260, 460 and 1200 sec., respectively. When a is the initial concentration of selenious acid (mol./l.), p the quantity of reduced selenious acid (equal to precipitated selenium) after time t (in sec.), k_1[*3] the rate constant (l. mol^{-1} sec^{-1}), $t_{1/2}$ the half time (sec.), and the reaction is of the nth order with respect to selenious acid, this reaction can be expressed mathematically by

$$-\mathrm{d}(a-p)/\mathrm{d}t=\mathrm{d}p/\mathrm{d}t=k_1(a-p)^n \tag{1}$$

The solution of Eq. 1 is as follows,

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

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

[*2] Calculated from pH value.

[1] J. W. Mellor: "A Comprehensive Treatise on Inorg. and Theoret. Chem." Vol. X, S, Se, p. 699.

[*3] k_1 does not mean the rate constant of first order reaction, but the rate constant of the reduction of selenious acid in hydrochloric acid.

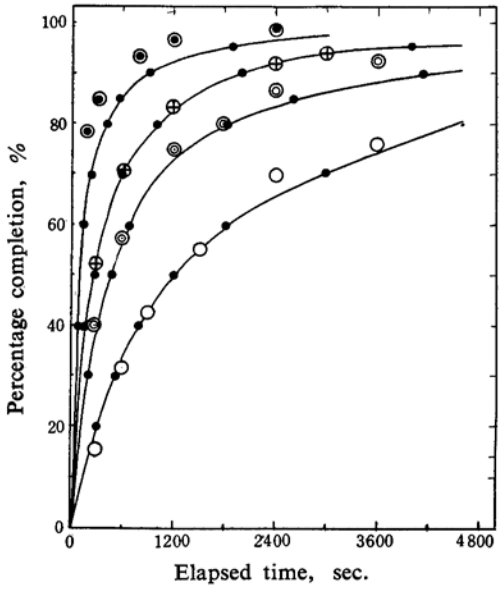

Fig. 1. H_2SeO_3 concn. dependence of the reduction of H_2SeO_3 in HCl at const. $[H^+]$ (0.49 g. ion/l.) and const. temp. (70°C).

- ◉ 0.0876 mol./l.
- ⊕ 0.0368 〃
- ◎ 0.0184 〃
- ○ 0.0086 〃
- • Calculated by Eq. 2, with n equal to 2.

$$t=\{a^{n-1}-(a-p)^{n-1}\}/\{k_1(n-1)\times(a-p)^{n-1}a^{n-1}\} \qquad (2)$$

If t is equal to $t_{1/2}$, p is equal to $a/2$. Making these substitutions for t and p in Eq. 2, the result is

$$t_{1/2}=(2^{n-1}-1)/\{k_1(n-1)a^{n-1}\} \qquad (3)$$

When the values of the initial concentration of selenious acid and the experimentally determined half time ($t_{1/2}$) are substituted for a and $t_{1/2}$ in Eq. 3, four equations are obtained;

$$1200=(2^{n-1}-1)/\{k_1(n-1)\times 0.0086^{n-1}\} \qquad \text{(i)}$$

$$460=(2^{n-1}-1)/\{k_1(n-1)\times 0.0184^{n-1}\} \qquad \text{(ii)}$$

$$260=(2^{n-1}-1)/\{k_1(n-1)\times 0.0368^{n-1}\} \qquad \text{(iii)}$$

$$100=(2^{n-1}-1)/\{k_1(n-1)\times 0.0876^{n-1}\} \qquad \text{(iv)}$$

Combining these equations, one can obtain the values of n which are 2.27, 1.82, 2.10, 2.05, 2.07 and 1.98. The mean value of n is 2.05, and from this it can be established that this reaction is one of second order with respect to selenious acid. As n is equal to 2, the values of k_1 can be calculated from the above four equations.

Temperature Dependence of the Reduction of Selenious Acid.—At constant initial concentration of selenious acid (0.0184 mol./l.) and constant hydrogen ion concentration (0.49 g. ion/l.), selenious acid in hydrochloric acid is reduced by sulfur dioxide, when the temperature is at 70, 60, 55 and 50°C. Fig. 2 shows the plot of the percentage completion against the elapsed time based upon the experimental data. As n is equal to 2, and the values of the initial concentration of selenious acid are known and the values of half time can be obtained from Fig. 2, upon making these substitutions for the values for n, a and $t_{1/2}$ in Eq. 3, the rate constants at 70, 60, 55 and 50°C are 0.118, 0.042, 0.020 and 0.012 l. mol^{-1} sec^{-1}, respectively.

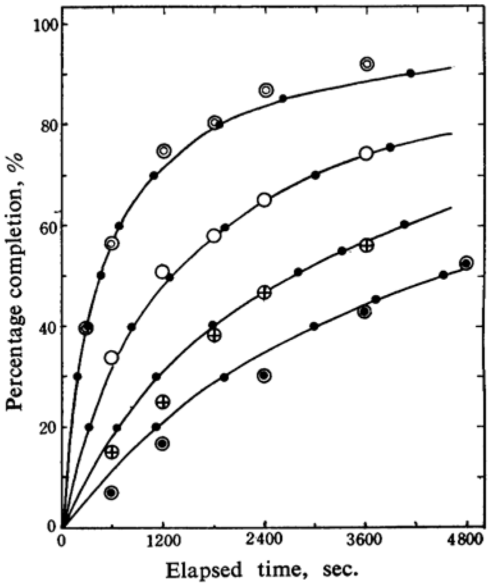

Fig. 2. Temperature dependence of the reduction of H_2SeO_3 at const. $[H_2SeO_3]$ (0.0184 mol./l.) and const. $[H^+]$ (0.49 g. ion/l.).

- ◎ 70°C
- ○ 60°C
- ⊕ 55°C
- ◉ 50°C
- • Calculated by Eq. 2, with n equal to 2.

The influence of temperature on reaction velocity can be derived by plotting the logarithm of the rate constant, $\log k_1$, against the reciprocal of the absolute temperature, $1/T$ (Fig. 3). As Fig. 3 shows that the experimental points fall on a straight line, the energy of activation E can be calculated from the value of the slope in Fig. 3.

The slope is equal to $-E/2.303\boldsymbol{R}$[2]. The slope of the straight line in Fig. 3 is equal to -5.35×10^3, and as $\boldsymbol{R}$ is taken as 1.987 cal. deg^{-1} mol^{-1}, it follows that for the reduction of selenious acid E is 24.5 kcal./mol. Moreover,

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[2] S. Glasstone, "Elements of Physical Chemistry", Maruzen, Tokyo (1958), p. 607.

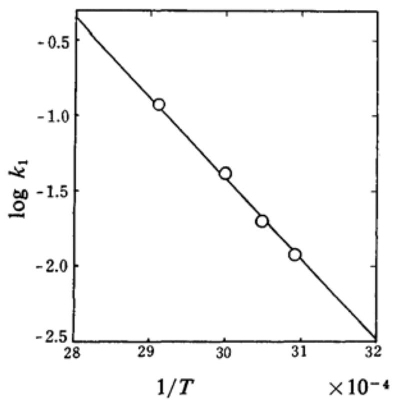

Fig. 3. Arrhenius' plot of the reduction of H_2SeO_3 by SO_2.

the rate constant k_1 is proportional to exp $(-E/\boldsymbol{R}T)$.

Hydrogen Ion Concentration Dependence of the Reduction of Selenious Acid.—At a constant initial concentration of selenious acid (0.0184 mol./l.), the constant temperature (60°C) and various hydrogen ion concentrations (0.26, 0.38, 0.49 and 0.96 g. ion/l.), the selenious acid in hydrochloric acid were reduced by sulfur dioxide. These results are shown in Fig. 4.

Rate constant k_1 can be obtained from Eq. 3. Plotting the rate constant against the square of hydrogen ion concentration, it is seen in Fig. 5 that the experimental points fall on a straight line.

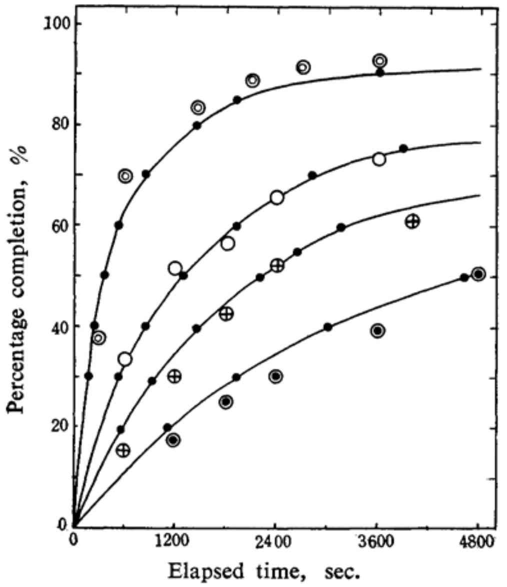

Fig. 4. $[H^+]$ dependence of the reduction of H_2SeO_3 at const. $[H_2SeO_3]$ (0.0184 mol./l.) and const. temp. (60°C).

◎ 0.96 g. ion/l.
○ 0.49 〃
⊕ 0.38 〃
◉ 0.26 〃
• Calculated by Eq. 2, with *n* equal to 2.

It is evident from Fig. 5 that rate constant k_1 is proportional to $[H^+]^2$.

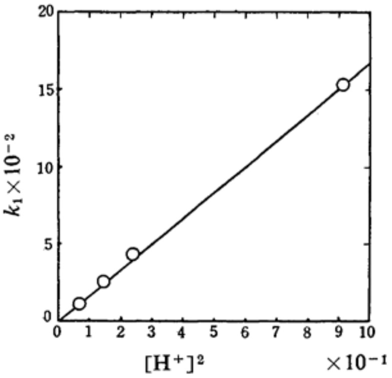

Fig. 5. Plot of k_1 against $[H^+]^2$.

When the temperature is equal to 60°C, hydrogen ion concentration is equal to 0.49 g. ion/l. and the initial concentration of selenious acid is equal to 0.0184 mol./l., the rate constant k_1 is evaluated to be 0.042 l. $mol^{-1}\ sec^{-1}$. When these values[*4] are adopted, the general Eq. 4 for rate constant can be derived, according to the above-mentioned temperature and hydrogen ion concentration dependence, that is,

$$k_1 = 2.054 \times 10^{15} \times [H^+]^2 \exp(-E/\boldsymbol{R}T) \quad (4)$$

where E is the energy of activation (24.5 kcal./mol.), $\boldsymbol{R}$ the gas constant (1.987 cal. deg^{-1} mol^{-1}) and T the absolute temperature.

Summary

(1) The reduction of selenious acid in hydrochloric acid by sulfur dioxide is a typical second order reaction with respect to selenious acid, while the reaction is of zero order with respect to sulfur dioxide because of the continuous passage of sulfur dioxide through a solution.

(2) The results obtained at 70, 60, 55 and 50°C (a=0.0184 mol./l., $[H^+]$=0.49 g. ion/l.) give a good Arrhenius plot, leading to the value of 24.5 kcal. mol^{-1} for the energy of activation.

(3) The rate constant of this reaction under a certain condition can be evaluated by the general equation,

$$k_1 = 2.054 \times 10^{15} \times [H^+]^2 \exp(-E/\boldsymbol{R}T)$$

where $[H^+]$ is hydrogen ion concentration, E, the energy of activation and T absolute temperature.

[*4] These experimental data are in good accordance with theoretical values (denoted by •) obtained from Eq. 2.

(4) The reduction of selenious acid in sulfuric acid, which will be published in a subsequent paper, is a reversible reaction. The above equation for the rate constant is utilized as a basic equation, in order to determine the rate constant in the forward direction of the reversible reaction.

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