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Kinetics of Oxygen Exchange between Selenite Ions and Water

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The rate of oxygen exchange between selenite ions and solvent water has been measured at 0°C over the pH range of 8.7—12.5. The rate of exchange, R, may be expressed by the rate law;

$$R = k_1[\mathrm{SeO_3}^{2-}] + k_2[\mathrm{HSeO_3}^-] + k_3[\mathrm{HSeO_3}^-]^2 + k_4[\mathrm{HSeO_3}^-][\mathrm{SeO_3}^{2-}].$$

The observed rates were analysed in order to obtain the values of the rate constants. The over-all exchange reaction shows a negative salt effect; this has been shown to be an equilibrium salt effect on the dissociation of the hydrogen selenite ion.

No kinetic study of oxygen exchange between selenite ions and water has ever been reported. Earlier qualitative studies[1] have revealed that selenite ions exchange their oxygen atoms with water very rapidly even in a strongly alkaline solution. As a part of the study of oxygen exchange between water and oxyanions of selenium, we have studied the exchange of selenite ions.

Experimental

Materials. Sodium selenite(Special grade, JIS) was used without further purification. Water enriched in oxygen-18 and guanidine hydrochloride were treated as has been described in a previous paper.[2] The other materials were of an analytical reagent grade and were used without further purification.

Procedure. The procedures were almost the same as those used in the previous work.[2] Exchange was started by diluting an isotopically-equilibrated solution of sodium selenite in oxygen-18 water with a relatively large amount of isotopically-normal water. The pH was adjusted by the addition of hydrochloric acid or a sodium hydroxide solution, and the ionic strength, by the addition of sodium

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[1] N. F. Hall and O. R. Alexander, *J. Amer. Chem. Soc.*, **62**, 3455 (1940); A. I. Brodskii and N. A. Vysotzkaya, *Zh. Fiz. Khim.*, **32**, 1521 (1958).

[2] A. Okumura and N. Okazaki, This Bulletin, **46**, 1080 (1973).

chloride. The reaction was carried out in an ice-water bath or in a low-temperature bath. At appropriate intervals, the reactant was precipitated by adding a barium chloride solution. For the runs at pH>11, care was taken to avoid contamination with atmospheric carbon dioxide. The water used for the preparation of the solution was boiled to exclude the dissolved carbon dioxide, and the operations were carried out in a nitrogen atmosphere freed from carbon dioxide. The precipitate, after being washed three times with absolute ethanol, was dried in an oven at 110°C, and then converted into carbon dioxide by the guanidine hydrochloride method.[3] The precipitate of barium selenite is not oxidized by air during the drying at 110°C. The isotopic analysis of the carbon dioxide was made on a Hitachi RMS-I-type mass spectrometer.

The rate of oxygen exchange in g atom per liter per unit of time was calculated by the relation;

$$R = -\frac{3[\mathrm{Se(IV)}][\mathrm{H_2O}]}{3[\mathrm{Se(IV)}]+[\mathrm{H_2O}]}\cdot\frac{1}{t}\cdot\ln\frac{O_t-O_\infty}{O_0-O_\infty}$$

where O_0, O_t, and O_∞ are the oxygen-18 atom per cent of the selenite ion at time 0, t, and infinity respectively, and where [Se(IV)] and [H_2O] are molar concentrations of selenite and water respectively. The McKay plots were linear over two half-periods.

For the analysis of the results, it is desirable to obtain the pK_2 values of selenious acid under the conditions of the kinetic runs. These were obtained by potentiometric titrations with a glass electrode.[4] The 0.053 M sodium selenite solution was titrated with 0.55 N hydrochloric acid with and without added sodium chloride, the values of the ionic strength at the half-neutralisation points being $I=0.56$ and 0.14 M respectively. The values of pK_2(at 0°C) obtained are $8.10_1\pm0.00_3$ at $I=0.56$ M, and $8.38_2\pm0.01_5$ at $I=0.14$ M.

Results and Discussion

pH Dependence of the Exchange Rate. Figure 1 shows the variation in the exchange rate with the pH at 0 °C and at a fixed total selenite concentration ([Se(IV)]=0.055−0.059 M). The exchange was studied at two different values of ionic strength, $I=0.16(\pm0.02)$ M and $I=0.54(\pm0.01)$ M. In the region of pH<9, plots of $\log R$ against pH for the runs at $I=0.54$ and 0.16 M are linear with slopes of 1.24±0.05 and 0.99±0.08 respectively (Fig. 2). On the other hand, above pH=11, the rate is practically independent of the pH.

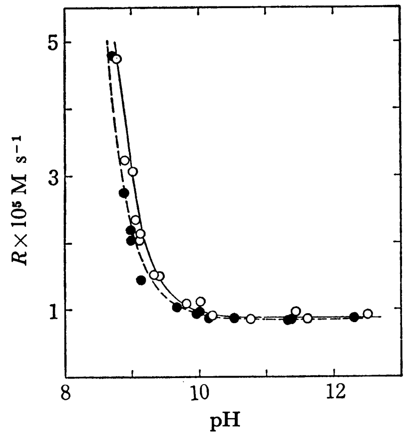

Fig. 1. Rate of oxygen exchange of selenite ions as a function of pH at 0°C. [Se(IV)]=0.055—0.059 M. Open circle: $I=0.16$ M, Solid circle: $I=0.54$ M. The curves show the calculated rates. Solid line: $I=0.16$ M, Broken line: $I=0.54$ M.

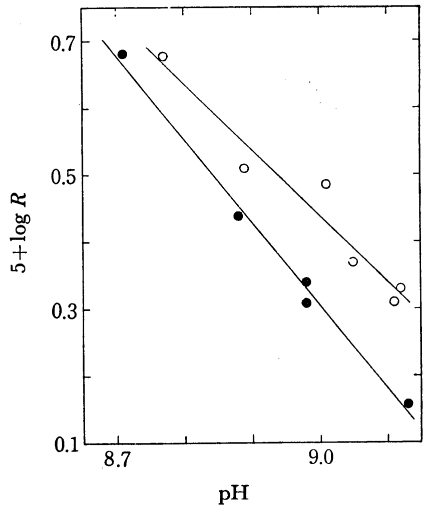

Fig. 2. Dependence of exchange rate on pH in the region of pH<9.1. Open circle: $I=0.16$ M, Solid circle: $I=0.54$ M.

To check the possibility of hydroxide-ion catalysis, the exchange reaction was studied in a strongly alkaline medium in the following way. A solution of sodium selenite was mixed with a solution of sodium hydroxide in oxygen-18 water in an ice-water bath. The mixed solution was 1.94 M in hydroxide ion and 2.21 M in sodium selenite. At appropriate intervals, a portion of the solution was removed and subjected to vacuum distillation to separate the water. The water thus obtained was analysed for its oxygen-18 content by the guanidine hydrochloride method. As a control, a solution containing an equivalent amount of sodium chloride instead of sodium hydroxide was also studied ([Se(IV)]=2.09 M). The rate observed were;

$$R(\mathrm{NaOH}) = (1.9\pm0.1)\times10^{-4}\ \mathrm{mol/l\,s},$$

and $$R(\mathrm{NaCl}) = (10.1\pm0.4)\times10^{-4}\ \mathrm{mol/l\,s}.$$

The value of R(NaOH) may be recalculated to the rate for [Se(IV)]=0.057 M by the observed first-order dependence on [Se(IV)]. The value thus obtained is 0.5×10^{-5} mol/l s, which compares well with the values obtained at pH=10—12 (see Fig. 1). These facts suggest the absence of hydroxide-ion catalysis.

Salt Effect. In the region of pH<9.5, the addition of sodium chloride exhibits a retarding effect on the exchange rate (see Fig. 1). The effect decreases with the increase in pH and above pH≃11 merges into the experimental errors. In Fig. 1, a plot at pH=8.98 and $I=0.54$ M was obtained with a solution the ionic strength of which was adjusted by the addition of sodium perchlorate instead of sodium chloride. The plot falls on a line with other plots. This fact

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[3] P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal Chem.*, **33**, 1906 (1961).

[4] A. Albert and E. P. Serjeant, "Ionization constants of acids and bases. A laboratory manual." Translated by S. Matsuura, Maruzen, Tokyo (1963).

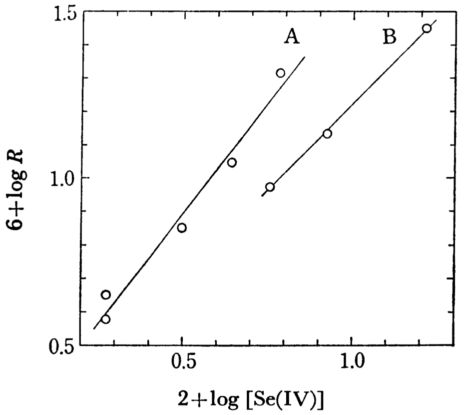

Fig. 3. Dependence of exchange rate on [Se(IV)]. $I=0.54$ M. A: pH=9.19, B: pH=10.1.

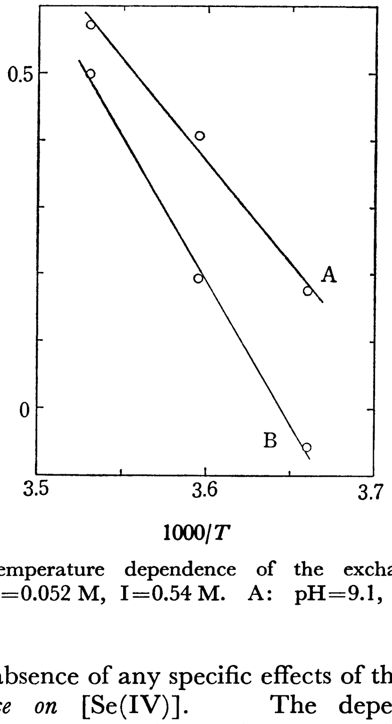

Fig. 4. Temperature dependence of the exchange rate. [Se(IV)]=0.052 M, I=0.54 M. A: pH=9.1, B: pH=10.1.

shows the absence of any specific effects of these anions.

Dependence on [Se(IV)]. The dependence of the exchange rate on the total concentration of selenite [Se(IV)] was studied at 0°C and at a constant ionic strength ($I=0.54$ M) for two fixed values of pH (9.19 and 10.1) (Fig. 3). These pH values are representative of the two pH regions of different rate-pH relationships. The observed rates were corrected for the difference in pH values (<0.05 pH). The slopes of the plots of $\log R$ against $\log\,[\mathrm{Se(IV)}]$ are 1.32 ± 0.08 for pH=9.19 and 1.04 ± 0.03 for pH=10.1.

Activation Energies. Because of the rapidity of the exchange reaction, the temperature dependence of the exchange rate could be studied only over a limited temperature range (0—10°C) (Fig. 4). In Fig. 4 the rates observed at pH=9.1 are corrected for the difference in pH values (<0.1 pH). The values of the activation energy were calculated to be;

$$E_a=14.0\pm0.9\ \text{kcal/mol, at pH}=9.1\ \text{and}\ I=0.54\ \text{M},$$

and

$$E_a=19.6\pm0.8\ \text{kcal/mol, at pH}=10.1\ \text{and}\ I=0.54\ \text{M}.$$

Analysis of the Exchange Rate. In the region of pH > *ca.* 10, where SeO_3^{2-} is the dominating ionic species and where the concentration of $HSeO_3^-$ is less than 1 per cent of the total selenite-ion concentration, the rate is independent of the pH and depends on the first power of the total selenite concentration. This fact, together with the finding that hydroxide ion catalysis is absent, suggests that the exchange occurs through the mechanism;

$$\mathrm{SeO^*{}_3^{2-} + H_2O \rightleftarrows SeO_3^{2-} + H_2O^*}. \tag{1}$$

In the region of pH<*ca.* 9, the observed kinetic order with respect to the [Se(IV)] of 1.32 at pH=9.2 suggests bimolecular mechanisms between selenite ions as important paths;

$$\mathrm{HSeO_3^- + HSeO_3^- \rightleftarrows Se_2O_5^{2-} + H_2O}, \tag{3}$$

$$\mathrm{HSeO_3^- + SeO_3^{2-} \rightleftarrows Se_2O_5^{2-} + OH^-}. \tag{4}$$

The occurrence of the pyroselenite ion in aqueous solutions of alkali hydrogen selenite (0.5—4 M) has been demonstrated by Raman spectroscopic investigation.[5] Moreover, SeO_3^{2-} being still the major species, exchange occurs through Path (1), and Path (2);

$$\mathrm{HSeO^*{}_3^- + H_2O \rightleftarrows HSeO_3^- + H_2O^*}, \tag{2}$$

should gain increasing importance with an increase in the biselenite-ion concentration. Thus, the rate law of the oxygen exchange of the selenite ion over the entire range studied may be written as;

$$\begin{aligned}\mathrm{R} &= k_1[\mathrm{SeO_3^{2-}}] + k_2[\mathrm{HSeO_3^-}] + k_3[\mathrm{HSeO_3^-}]^2\\ &\quad + k_4[\mathrm{HSeO_3^-}][\mathrm{SeO_3^{2-}}].\end{aligned} \tag{I}$$

In the region of pH>10, we may, to a good approximation, ignore the occurrence of the k_2 and k_3 paths. The observed [Se(IV)] dependence of 1.04 at pH=10.1 suggests some contribution to the exchange of the bimolecular path, k_4. The rate equation may be simplified as;

$$R = k_1[\mathrm{SeO_3^{2-}}] + k_4[\mathrm{SeO_3^{2-}}][\mathrm{HSeO_3^-}],$$

$$\text{or}\quad R/[\mathrm{SeO_3^{2-}}] = k_1 + k_4[\mathrm{HSeO_3^-}].$$

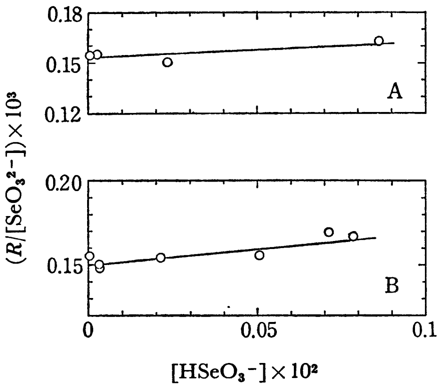

Fig. 5. Evaluation of the rate constants k_1 and k_4. A: $I=0.16$ M, B: $I=0.54$ M.

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[5] A. Simon and R. Paetzold, *Z. Anorg. Allgem. Chem.*, **303**, 46 (1960).

Fig. 5 shows the plots of $(R/[SeO_3^{2-}])$ against $[HSeO_3^-]$ for I=0.16 and 0.54 M. The values of $[SeO_3^{2-}]$ and $[HSeO_3^-]$ were calculated by using the appropriate values of pK_2 (see experimental part). From the intercepts and the slopes of the plots, the values of k_1 and k_4 have been obtained as;

$$k_1(0.16\,\mathrm{M})=(0.15_3\pm0.00_2)\times10^{-3}\,\mathrm{s}^{-1},$$
$$k_1(0.54\,\mathrm{M})=(0.15_0\pm0.00_2)\times10^{-3}\,\mathrm{s}^{-1},$$
$$k_4(0.16\,\mathrm{M})=(0.10\pm0.04)\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1},$$
$$k_4(0.54\,\mathrm{M})=(0.21\pm0.03)\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1}.$$

As may be expected, the k_1 path is free from the salt effect and the k_4 path shows a positive salt effect.

By using the $[Se(IV)]=[HSeO_3^-]+[SeO_3^{2-}]$ relation, Eq. (I) may be rewritten in the form;

$$(R-k_1[SeO_3^{2-}])/[HSeO_3^-] = (k_2+k_4[Se(IV)]) + (k_3-k_4)[HSeO_3^-]. \qquad \text{(II)}$$

Fig. 6 shows the plots of $(R-k_1[SeO_3^{2-}])/[HSeO_3^-]$ against $[HSeO_3^-]$ at a constant [Se(IV)] for two values of the ionic strength. The least-squares treatment yields;

$$(k_2+k_4[Se(IV)])=(0.68\pm0.16)\times10^{-3}\,\mathrm{s}^{-1},$$
and $(k_3-k_4)=(1.16\pm0.16)\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$,

for I=0.16 M, and

$$(k_2+k_4[Se(IV)]) = (1.05\pm0.14)\times10^{-3}\,\mathrm{s}^{-1},$$
and $(k_3-k_4) = (1.54\pm0.25)\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$,

for I=0.54 M. By using the values of k_4 obtained above, k_3 may be evaluated from the values of k_3-k_4 as;

$$k_3(0.16\,\mathrm{M}) = (1.3\pm0.2)\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1},$$
and $k_3(0.54\,\mathrm{M}) = (1.8\pm0.3)\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$,

As it is expected that the value of k_2 is only a small fraction of the value of $k_2+k_4[Se(IV)]$, it is unadvisable to evaluate k_2 from $k_2+k_4[Se(IV)]$. By using the relation, $[HSeO_3^-]=[Se(IV)]/(1+(K_2/a_{H^+}))$, Eq. (II) may be rewritten in the form;

$$(R-k_1[SeO_3^{2-}])/[HSeO_3^-] = k_2 + S[Se(IV)], \qquad \text{(III)}$$
$$S=(k_3a_{H^+}/(K_2+a_{H^+}))+(k_4K_2/(K_2+a_{H^+})).$$

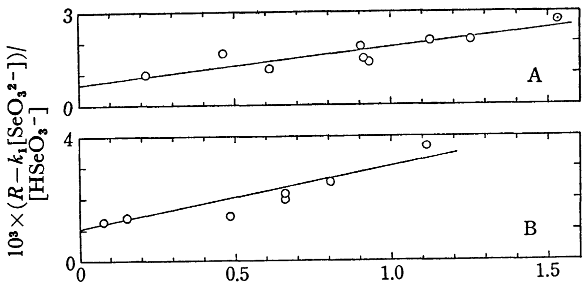

Fig. 6. $(R-k_1[SeO_3^{2-}])/[HSeO_3^-]$ as a function of $[HSeO_3^-]$. A: I=0.16 M, B: I=0.54 M.

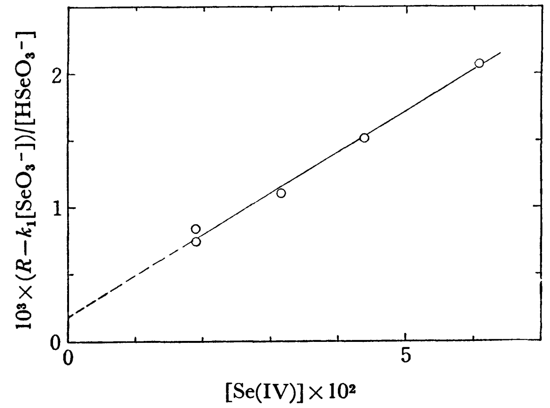

Fig. 7. Evaluation of the rate constant k_2 at I=0.54 M.

Figure 7 shows a plot of $(R-k_1[SeO_3^{2-}])/[HSeO_3^-]$ against [Se(IV)] at a constant pH(9.19) and ionic strength (0.54 M); here the data in Fig. 3 are replotted according to the equation above. The least-squares treatment of the plot yields the values;

$$k_2(0.54\,\mathrm{M}) = (0.19\pm0.04)\times10^{-3}\,\mathrm{s}^{-1},$$
$$S(0.54\mathrm{M}) = (0.31\pm0.01)\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1}.$$

As Path (2) may be expected to be free from any kinetic salt effect, the rate constant, k_2, at I=0.16 M should have almost the same value as k_2(0.54 M).

The values of k_4 calculated from the values of k_2 and $k_2+k_4[Se(IV)]$ are $k_4(0.16\,\mathrm{M})=0.09\times10^{-1}$ and $k_4(0.54\,\mathrm{M})=0.15\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$. The value of k_3(0.54 M) may also be calculated from the values of k_4 and of the slope, S, of Eq. (III). The result is $k_3(0.54\,\mathrm{M})=1.5\times10^{-1}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$. These values are in satisfactory agreement with the values of k_3 and k_4 obtained above. This fact gives evidence of the self-consistency of this analysis.

The values of the rate constants obtained are summarized in the following table. By using the rate law (I) and the values of the rate constants, the rates of oxygen exchange are recalculated and shown as curves in Fig. 1. The agreement of the calculated rates with the observed rates is satisfactory except at the acidic end of the curve for I=0.54 M.

The reactivities of the hydrogen-selenite and selenite ions towards water are almost equal, the former being somewhat larger. The hydrogen-selenite ion is about ten times as reactive as the selenite ion towards the

TABLE 1. THE VALUES OF RATE CONSTANTS AT 0°C

Exchange path	Rate const. (unit)	Ionic strength	
		0.16 M	0.54 M
$SeO_3^{2-}+H_2O \rightleftarrows$	$k_1(\mathrm{s}^{-1})$	0.15×10^{-3}	0.15×10^{-3}
$HSeO_3^-+H_2O \rightleftarrows$	$k_2(\mathrm{s}^{-1})$	$0.2\ \times10^{-3}$	$(0.2\ \times10^{-3})$
$HSeO_3^-+HSeO_3^- \rightleftarrows Se_2O_5^{2-}+H_2O$	$k_3(\mathrm{M}^{-1}\mathrm{s}^{-1})$	$1.3\ \times10^{-1}$	$1.8\ \times10^{-1}$
$HSeO_3^- + SeO_3^{2-} \rightleftarrows Se_2O_5^{2-}+OH^-$	$k_4(\mathrm{M}^{-1}\mathrm{s}^{-1})$	$0.1\ \times10^{-1}$	$0.2\ \times10^{-1}$

hydrogen-selenite ion. This is in part due to the electrostatic repulsion between the reactants.

It may be seen from the table that none of the paths, (1)—(4), show a negative salt effect. Thus, the negative salt effect observed for the over-all oxygen exchange rate cannot be attributed to a kinetic origin. It must be due to an equilibrium salt effect on the dissociation of the biselenite ion. An increase in the ionic strength increases the dissociation of the biselenite ion and reduces the concentration of the reactive species, $HSeO_3^-$. The negative salt effect observed for the exchange of selenite2) probably has the same origin.

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