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Kinetics of Oxygen Exchange between Selenate Ions and Water

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The rate of oxygen exchange between selenate ions and solvent water has been measured by using oxygen-18 as a tracer. At 30°C in the concentration range of $[H_2SeO_4]=0.57$—1.5 M, and at 80°C in the region of pH$=1.0$—2.3, the rate may be expressed as $R=k_1[H^+][HSeO_4^-]$. The values of the energy and entropy of activation are 23.1 kcal/mol and -5.0 e.u.(80°C) at pH$=1.12$, and 21.8 kcal/mol and -9.9 e.u.(30°C) at $[H_2SeO_4]=1.64$ M. An A-2 mechanism has been suggested for this path. Above *ca* 1.5 M H_2SeO_4, an additional rate term proportional to $[H_2SeO_4]^2$ comes into play.

Oxygen exchange between oxyanions and water has been the subject of many investigations, but the nature of the reaction is not fully understood. The kinetics of the oxygen exchange of oxyanions of typical elements of the fourth period has, except for that of bromine,[1] received hitherto relatively little attention. For a better understanding of the nature of the reaction, it seems desirable to obtain information on the exchange behaviour of oxyanions of these elements. To this end, we have studied the oxygen exchange reactions between oxyanions of selenium and water.

Experimental

Materials. Water enriched in oxygen-18(1.8 atom%) was obtained from a fractionating column of this laboratory. It was refluxed with alkaline permanganate, distilled three times, and used without normalizing its deuterium content (<1 atom %). The selenic acid (Especially pure) was used without further purification. It contained 98% (by weight) of selenic acid (as analysed by the hydrazine method[2]) and 1.7% of selenious acid (as analysed by the permanganate method[3]). The absence of a catalytic effect of selenious acid on the oxygen exchange of selenic acid has been checked by preliminary experiments. The results will be given in a later section. Guanidine hydrochloride (Special grade, JIS) was recrystallized from absolute methanol, dried at 110°C, and stored in a descicator. All the other chemicals were of an analytical-reagent grade and were used without further purification.

Procedure. The solutions used for kinetic runs in the pH region were prepared as follows. Weighed amounts of selenic acid and oxygen-18 water were sealed in a glass ampoule, and the ampoule was heated for *ca.* 2 hr at 100°C to equilibrate the oxygen-18 content of selenic acid with that of the water. This solution was used as a stock solution. In a measuring flask (25 ml), a weighed amount of the isotopically-equilibrated solution was diluted with water of a normal isotopic content to 25 ml, proper amounts of sodium perchlorate and of sodium hydroxide or perchloric acid being added to adjust the ionic strength and the pH of the solution. A portion of the solution was analysed to check its composition. The pH values of the solutions were measured with Hitachi-Horiba M-5- or F-5-type pH meter. For the runs in the more acidic region ($[H_2SeO_4]>0.5$ M), the following procedure was chosen to minimize the induced exchange upon mixing. Selenic acid was added to oxygen-18 water which had been frozen in a dry ice-ethanol bath, and the mixture was caused to melt in an ice-water bath. Even with this procedure, the zero time exchange amounted to *ca.* 20% of the total exchange. The concentrations of selenic acid and hydrogen ion in the solution were determined by titration. The amount of water in the solution was determined by density measurement.

Portions of the solution were sealed in glass ampoules and

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[1] T. C. Hoering, R. C. Butler, and H. O. McDonald, *J. Amer. Chem. Soc.*, **78**, 4829 (1956); M. Anbar and S. Guttmann, *ibid.*, **83**, 4741 (1961); H. Gamsjäger, A. Grütter, and P. Baertschi, *Helv. Chim. Acta*, **55**, 781 (1972); M. Anbar and H. Taube, *J. Amer. Chem. Soc.*, **80**, 1073 (1958).

[2] B. Blanka, P. Hudec, P. Mosna, and J. Touzim, *Collection Czech. Chem. Commun.*, **28**, 3434 (1963).

[3] S. Barabas and W. C. Cooper, *Anal. Chem.*, **28**, 129 (1956).

placed in a constant-temperature bath. At appropriate intervals an ampoule was removed and cooled rapidly, and the selenate ions were precipitated by adding a barium chloride solution. The precipitate was separated by centrifuge washed three times with absolute ethanol, and dried at 110°C. It was then converted into carbon dioxide by heating it at 400°C for 1 hr with guanidine hydrochloride in a borosilicate glass tube. This method[4] was originally proposed for the oxygen-18 analysis of water and of acid phosphates, and the reaction involved in the method is a hydrolytic one. In the present case, however, the reaction is of an oxidation-reduction type. The conversion of selenate oxygen into carbon dioxide was$>$60%. The carbon dioxide, being freed from ammonia and water vapour, was analysed on a Hitachi RMS-I-type mass spectrometer.

The rate of oxygen exchange in g atom per liter in unit of time was calculated by means of the formula:

$$R = -\frac{4[\mathrm{Se(VI)}][\mathrm{H_2O}]}{4[\mathrm{Se(VI)}]+[\mathrm{H_2O}]}\cdot\frac{1}{t}\cdot\ln(1-F),$$

$$F = (O_0 - O_t)/(O_0 - O_\infty),$$

where O_0, O_t, and O_∞ are the ^{18}O atom% of the selenate oxygen at time zero, t, and infinity respectively, and where [Se(VI)] and [H_2O] are the molar concentrations of the selenate ion and water respectively. For each run, 4 or 5 samples were taken at intervals over about two half-lives, and the infinity value was taken after ten half-lives. The McKay plots were satisfactorily linear over two half-lives.

Results and Discussion

Oxygen Exchange in the pH Region. This has been studied at 80°C in the pH region of 1.0—2.3 (Fig. 1). The total selenate concentrations were kept in the 0.064—0.068 M range, and the pH values were adjusted by the addition of a small amount of perchloric acid or of a sodium hydroxide solution. The ionic strengths of the solutions were not adjusted and were in the 0.08—0.16 M range. The pH values were measured at 80°C with solutions of the same compositions (but without oxygen-18 label) as those of the kinetic runs. Figure 1 shows that the pH dependence changes from first-order(pH$<$1.4) to second-order(pH$>$2.00) with the increase in the values of pH. The straight line through the four points on the left of the figure has a slope of $-(0.95\pm0.04)$, and the line through the three points on the right, one of $-(2.01\pm0.11)$. This change in kinetic order occurs in the region of the pK_2 value of selenic acid, which has been determined by potentiometric titrations with a glass electrode to be 1.93±0.01(at 80°C).

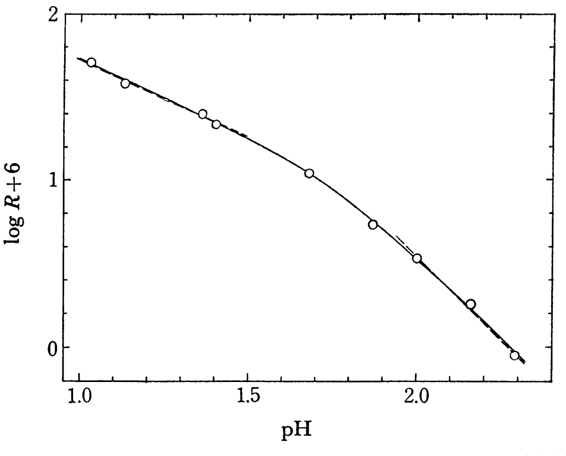

Fig. 1. Dependence of exchange rate on pH at 80 °C ([Se(VI)]=0.064—0.068 M).

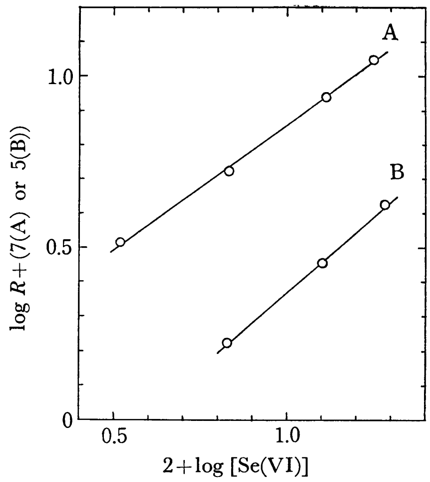

Fig. 2. Dependence of exchange rate on total concentration of selenate [Se(VI)] at 80 °C. The ordinate is $7+\log R$ for A(pH=2.03) and $5+\log R$ for B(pH=1.23).

The dependence of the exchange rate on the total selenate concentration has been studied at two fixed pH values at 80°C. The observed rates were corrected for small differences in pH values ($<$0.05) by the observed pH dependence. Plots of log R against log [Se(VI)] yield straight lines with slopes of 0.88±0.02 at pH=1.23(I=0.61 M) and of 0.73±0.01 at pH=2.03(I=1.15 M) (Fig. 2). It may be inferred that the exchange reaction is first-order with respect to the total selenate concentration over the entire pH range studied.

These results may be best interpreted in terms of the rate law:

$$R = k[\mathrm{H^+}][\mathrm{HSeO_4^-}] = k[\mathrm{H^+}][\mathrm{Se(VI)}]/(1+(K_2/[\mathrm{H^+}]))$$

$$\simeq k[\mathrm{H^+}][\mathrm{Se(VI)}], \qquad [\mathrm{H^+}]>K_2, \qquad (1)$$

$$\simeq (k/K_2)[\mathrm{H^+}]^2[\mathrm{Se(VI)}], \qquad [\mathrm{H^+}]<K_2. \qquad (1')$$

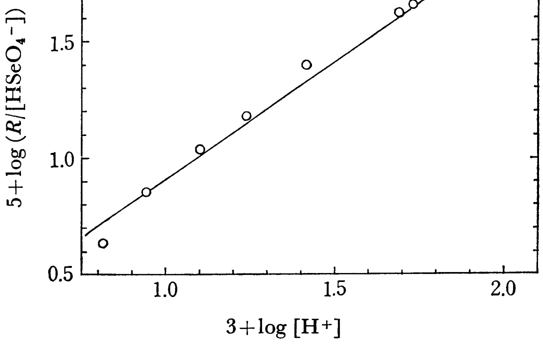

Fig. 3. R/[$HSeO_4^-$] as a function of log[H^+] at 80°C.

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

Fig. 3 shows a plot of log (R/[$HSeO_4^-$]) against log [H^+]. The straight line through the points has a slope of 1.00±0.03. The exchange reaction is first-order in both hydrogen-ion and biselenate-ion concentrations, which is in agreement with the rate law. The least-squares treatment of the plots yields the rate constant of $k=(8.2\pm0.8)\times10^{-3}\ \mathrm{l\ mol^{-1}\ s^{-1}}$. In the above treatment, the concentrations of the selenate ion species at each pH value were calculated from [Se(VI)] and $K_2=a_{H^+}\cdot[SeO_4^{2-}]/[HSeO_4^-]$, and the values of K_2 by the formula:

$$\mathrm{p}K_2^\circ = \mathrm{p}K_2 + \log (f_{SeO_4^{2-}}/f_{HSeO_4^-}),$$

where $\mathrm{p}K_2^\circ$ is the thermodynamic dissociation constant and where f's are the activity coefficients. The value of $\mathrm{p}K_2^\circ$ at 80°C was obtained from Ghosh and Nair's results[5] by extrapolation, and the values of the activity coefficients were estimated by means of the Debye-Hückel equation by using the ion-size parameters tabulated by Kielland.[6] Succesive approximations yielded the $\mathrm{p}K_2$ values of 2.03—1.93 for I=0.08—0.16 M, which are consistent with the experimentally-determined value; they were used to calculate [$HSeO_4^-$].

The temperature dependence of the exchange rate has been studied at two fixed pH values, 1.12(at 60, 80, and 95 °C) and 1.81(80, 100, and 120 °C) (Fig. 4). These pH values were measured at room temperature and correspond to pH values of 1.36 and 2.30 at 80 °C. A batch of a solution with a fixed pH was divided into three portions, and each portion was brought to the appropriate reaction temperature. Thus, the observed temperature variation in the exchange rate includes a contribution from the variation in the pH with the temperature. The activation parameters were calculated in the usual way to be $E_a=23.10\pm0.19$ kcal/mol and $\Delta S^{\neq}=-5.0\pm0.6$ e.u.(80 °C) at pH=1.12 and $E_a=17.18\pm0.17$ kcal/mol and $\Delta S^{\neq}=-23.4\pm0.5$ e.u.(80 °C) at pH=1.81. At pH=1.12, where the solution consists of aqueous selenic acid plus a small amount of perchloric acid, the dissociation of the biselenate ion changes little with the pH and contributes only a small fraction to the total hydrogen-ion concentration. Under these circumstances, the temperature variation in log R measures the variartion of log k with the temperature (Eq. (1)). On the other hand, at pH=1.81(buffer region), the temperature variation in log R may be expressed from Eq. (1′) as;

$$\frac{\mathrm{d}\log R}{\mathrm{d}T}=\frac{\mathrm{d}\log k}{\mathrm{d}T}-\frac{\mathrm{d}\log K_2}{\mathrm{d}T}+2\frac{\mathrm{d}\log a_{H^+}}{\mathrm{d}T}-2\frac{\mathrm{d}\log f_{H^+}}{\mathrm{d}T}$$

and the variation of a_{H^+} at a constant buffer ratio as;

$$\frac{\mathrm{d}\log a_{H^+}}{\mathrm{d}T}=\frac{\mathrm{d}\log K_2^\circ}{\mathrm{d}T}-\frac{\mathrm{d}\log f_{SeO_4^{2-}}}{\mathrm{d}T}+\frac{\mathrm{d}\log f_{HSeO_4^-}}{\mathrm{d}T}$$

The $\mathrm{d}\log f/\mathrm{d}T$'s terms may be ignored as compared with $\mathrm{d}\log K_2/\mathrm{d}T$.[7] Therefore,

$$E_a = E_a^\circ - \Delta H + 2\Delta H^\circ \simeq E_a^\circ + \Delta H^\circ,$$

where E_a° is the true activation energy of the exchange reaction and where ΔH° is the enthalpy of dissociation of the biselenate ion. The value of ΔH° is −5.70±0.2 kcal/mol.[5] Thus, the discrepancy between the activation energies at the two pH values seems quite reasonable.

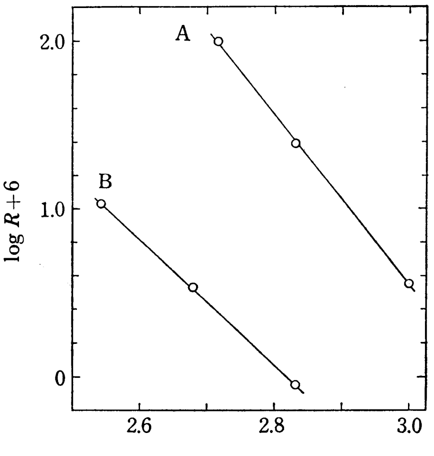

Fig. 4. Temperature dependence of exchange rate in the pH region. A: pH=1.36, [Se(VI)]=0.068 M, B: pH=2.30, [Se(VI)]=0.067 M.

The effect of the ionic strength has been studied at 80°C, pH=1.33, and [Se(VI)]=0.064 M, with solutions of I=0.82, 0.61, and 0.087 M. The observed rates were 1.47, 1.67, and 2.36×10^{-5} mol/l s respectively. The exchange reaction shows a negative salt effect which is probably due to an equilibrium salt effect on the dissociation of the biselenate ion.

The effect of selenious acid on the exchange rate is shown in the following table.

Table 1. The effects of selenious acid on the oxygen exchange rate of selenic acid at 80°C

Composition of the solution, M×10^2		pH	R(mol/l s)×10^5
[Se(VI)]	[Se(IV)]		
6.77	0.662	1.39	2.18±0.02
6.38	0	1.40	2.20±0.01
3.09	0.295	1.61	0.0391±0.0003
3.29	0	1.61	0.0370±0.0001

Oxygen Exchange in the Region, [H_2SeO_4]=0.56—5.46 M. Figure 5 shows a plot of log R against the logarithm of the total selenic acid concentration, log [Se(VI)], in the region of [Se(VI)]=0.56—5.46 M at 30°C. It may be seen that the [Se(VI)] dependence is nearly second-order up to 1.6 M, and approximately fourth-order above 3.8 M. As selenic acid is almost completely ionized into hydrogen and biselenate ions in this region, the concentrations of each of these ions may be taken to be proportional to [Se(VI)]. Thus, the rate law of the exchange reaction may be written;

$$R = k_1[H^+][HSeO_4^-] + k_2[H^+]^2[HSeO_4^-]^2. \qquad (2)$$

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5) R. Ghosh and V. S. K. Nair, *J. Inorg. Nucl. Chem.*, **32**, 3041 (1970).

6) J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

7) R. G. Bates, "Determination of pH, Theory and Practice", John Wiley and Sons, New York, (1965), p. 116.

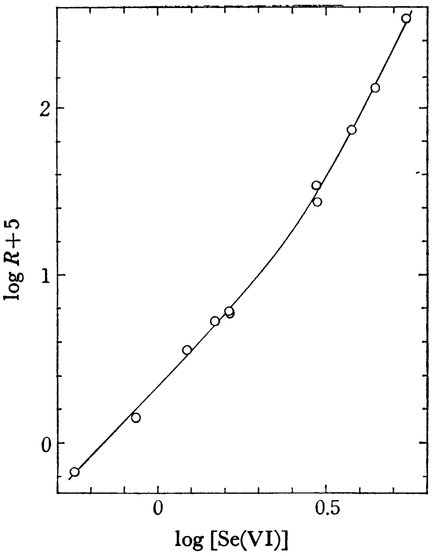

Fig. 5. Rate of oxygen exchange of selenic acid as a function of total concentration of selenic acid at 30°C.

The k_2 term may be interpreted as a bimolecular path involving two selenic acid molecules.

The dependence of the exchange rate on [Se(VI)] at a fixed hydrogen ion concentration has been studied at $[H^+]=3.92$ and 8.7 M. At $[H^+]=3.92$ M, [Se(VI)] was varied between 0.32 and 1.96 M by replacing a part of the selenic acid with an equivalent quantity of perchloric acid. The plot of log R against log[Se(VI)] is linear, with a slope of 1.09±0.03 at 60°C (Fig. 6–A). At $[H^+]=8.7$ M, selenic acid was replaced by an equivalent quantity of sulfuric acid, which has almost the same acid strength. In this case, the exchange was followed by measuring the decrease in the oxygen–18 content of water. After appropriate reaction times, about 70% of the water in the solution was recovered by the freeze-dry method and was analysed by the guanidine hydrochloride method. It had been confirmed preliminarily that no exchange of oxygen atoms of sulfuric acid occurs in these systems. Figure 6–B gives a plot of log R against log [Se(VI)] at 30°C. The observed rates were normalized to a hydrogen-ion concentration of 8.7 M.

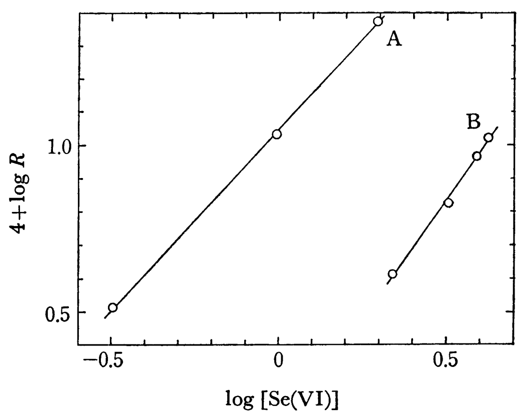

Fig. 6. Dependence of exchange rate on total concentration of selenic acid at constant hydrogen ion concentration.
A: $[H^+]=3.92$ M, 60°C; B: $[H^+]=8.7$ M, 30°C.

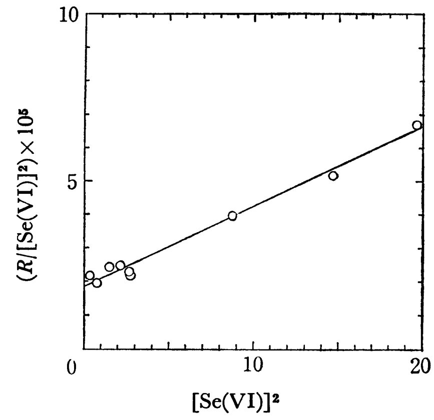

Fig. 7. $R/[Se(VI)]^2$ as a function of $[Se(VI)]^2$ at 30°C.

The least-squares treatment of the plots gives a straight line with a slope of 1.5±0.1. These results support the rate law given in Eq. (2).

Walrafen[8] has studied quantitatively the ionic species present in aqueous selenic acid by the Raman spectroscopic method. According to his results, the concentration of the H_2SeO_4 molecule is practically zero below *ca* 11 M, and from Fig. 3 of his paper, it may be estimated that, up to *ca* 4 M, the concentration of the selenate ion $[SeO_4^{2-}]$ is about three tenths of the total selenic acid concentration. Thus,

$$[HSeO_4^-] = [Se(VI)] - [SeO_4^{2-}] \simeq 0.7\,[Se(VI)],$$

$$[H^+] = [HSeO_4^-] + 2[SeO_4^{2-}] \simeq 1.3[Se(VI)],$$

and the rate law (2) becomes;

$$R/[Se(VI)]^2 = 0.91\,k_1 + 0.828\,k_2[Se(VI)]^2.$$

In Fig. 7, the data shown in Fig. 5 are replotted according to this equation, the points at [Se(VI)]= 5.64 and 2.99 M being ignored. The least-squares treatment yields the rate constants;

$$k_1 = (2.0_1 \pm 0.0_1) \times 10^{-5}\ \text{l/mol s}\quad (30°\text{C}),$$

$$k_2 = 0.3 \times 10^{-5}\ \text{l}^3/\text{mol}^3\,\text{s}\quad (30°\text{C}).$$

From the values of $k_1(=8.2\times 10^{-3}$ l/mol s) and the activation energy(=23.10 kcal/mol) obtained in the pH region at 80°C, the rate constant at 30°C is calculated to be 3.6×10^{-5} l/mol s, which is in satisfactory agreement with the above value. This fact suggests that the exchange reaction has the same mechanism in both the pH and molar regions.

The temperature dependence of the exchange rate in the molar region has been studied at [Se(VI)]= 1.64 M and at 30, 40, and 50°C (Fig. 8). The energy and entropy of activation are calculated to be E_a= 21.82±0.11 kcal/mol and $\Delta S^{\neq}=-9.9\pm 0.4$ e.u.(30°C).

Mechanisms of the Exchange Reaction. The second-order rate term, $k_1[H^+][HSeO_4^-]$, suggests the following mechanism;

$$H^+ + HSeO_4^- \rightleftarrows H_2SeO_4, \tag{3}$$

$$H_2SeO_4^* + H_2O \rightleftarrows H_2SeO_4 + H_2O^*, \tag{4}$$

$$\text{or}\quad H_2SeO_4 \rightleftarrows H_2O + SeO_3. \tag{5}$$

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[8] G. E. Walrafen, *J. Chem. Phys.*, **39**, 1479 (1963).

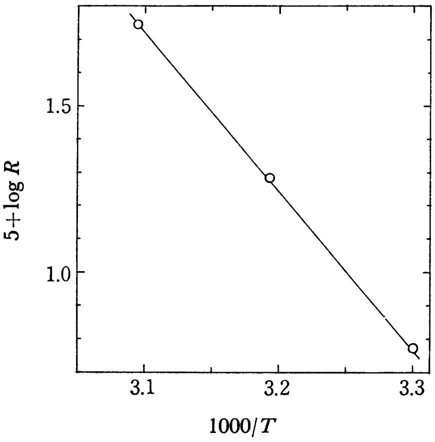

Fig. 8. Temperature dependence of exchange rate at [Se(VI)]=1.64 M.

The negative values of $\Delta S^{\neq}$ obtained for the reaction favour the bimolecular path (4).

Bunton and Hendy[9] have studied the acid hydrolysis of the methyl selenate ion. In contrast to the analogous reaction of the alkyl sulfate ion, the reaction is characterized by a negative value of the entropy of activation (−27 e.u.) and a relatively small deuterium solvent effect ($k_{D_2O}/k_{H_2O}=1.36$), and by a linear dependence of the hydrolysis rate on the hydrogen ion concentration. On the basis of these facts, these authors suggests an A–2 mechanism for the hydrolysis of the methyl selenate ion. Our results are not conclusive at present, but in view of the well-known analogy between the mechanisms of the oxygen exchange of oxyanions and the hydrolysis of its simple alkyl esters, it is probable that the oxygen exchange of the biselenate ion also proceeds through an A–2 mechanism (Path (4)). It is interesting to note that the plot of log(R/[Se(VI)]) against Hammett's acidity function $-H_0$ of selenic acid[10] gives a straight line with a slope of 0.66±0.01 over the entire range of acidity studied (up to 5.46 M, at 30 °C).

The fourth-order rate term, $k_2[H^+]^2[HSeO_4^-]^2$, which gains importance with an increase in the concentration of selenic acid, may be interpreted as a bimolecular path between two selenic acid molecules;

$$H_2SeO_4 + H_2SeO_4 \rightleftarrows H_2Se_2O_7 + H_2O.$$

The occurrence of $H_2Se_2O_7$ in water-free selenic acid has been suggested by Raman-spectroscopic and conductivity measurements.[11]

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[9] C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, **1963**, 3130,

[10] D. H. McDaniel and L. H. Steinert, *J. Amer. Chem. Soc.*, **88**, 4826 (1966).

[11] R. Paetzold and H. Amoulong, *Z. Anorg. Allgem. Chem.*, **343**, 70 (1966).