575. *Tracer Studies in Ester Hydrolysis. Part XII.* Dimethyl Selenate.*

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Hydrolysis of dimethyl selenate to methyl hydrogen selenate is very rapid in water, but can be followed kinetically in aqueous dioxan. Both hydrogen and hydroxide ion speed the reaction. Hydrolysis of the methyl selenate ion in aqueous alkali is fast, and in water slow. The rate of the acid-catalysed hydrolysis is approximately proportional to the acid concentration and is increased by addition of dioxan. The selenium–oxygen bond is broken in both stages of hydrolysis, and the suggested mechanisms involve nucleophilic attack upon the esters or their conjugate acids.

The selenium–oxygen bond is broken in both stages of the hydrolysis of dimethyl selenate (Table 1):

$$\mathrm{MeO{-}\!\vdots\, SeO_2{\cdot}OMe} \xrightarrow{\mathrm{H_2O}} \mathrm{H^+ + {}^-O{-}SeO_2\,\vdots\!{-}OMe} \xrightarrow{\mathrm{H_2O}} \mathrm{HSeO_4^- + MeOH}$$

The reactions are therefore very different from the hydrolyses of dialkyl sulphates,

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* Part XI, *J.*, 1963, 627.

where the alkyl–oxygen bond is broken,[1] and of alkyl hydrogen sulphates, where the sulphur–oxygen bond is broken in acid and the alkyl–oxygen bond in alkaline solution.[2]

TABLE 1.

Bond fission.

In $H_2{}^{18}O$ at 25·1° unless specified. Isotopic abundance N in atom % excess.

Reagent	0·2M-$HClO_4$		6M-$HClO_4$		M-NaOH
N_{H_2O}	0·80	0·90	0·60	0·60	0·75
N_{MeOH}	0·00	0·00 *	$0{\cdot}01_6$,†	$0{\cdot}01_9$ †‡	0·025

* In dioxan–water 90·8 : 9·2 v/v. † At 0°. ‡ Control expt. with MeOH.

In water the first stage of the hydrolysis of dimethyl selenate is fast and the second slow; the position is reversed in aqueous dioxan. The two stages will be discussed separately.

Hydrolysis of Methyl Hydrogen Selenate.—Addition of dimethyl selenate to water gives an immediate increase in conductivity to the value expected for a monobasic strong acid; there is then a very slow change to the conductivity of an equivalent solution of selenic acid (see Experimental section).

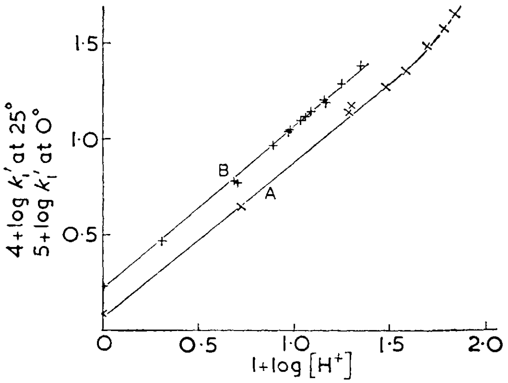

FIG. 1. Hydrolysis of the methyl selenate ion in aqueous perchloric acid (A) at 0° and (B) 25·1°.

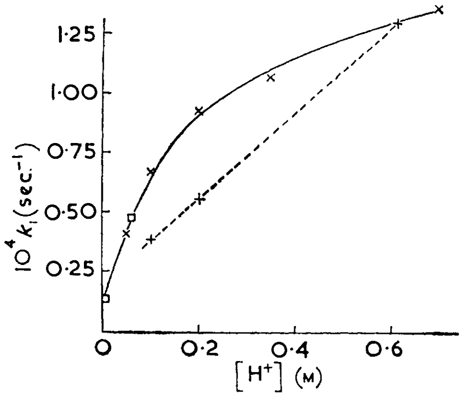

FIG. 2. Hydrolysis of dimethyl selenate in dioxan–water 90·8 : 9·2 v/v at 25·1°.

□ Conductimetry. × Titrimetry. For points on the broken line, $[HClO_4] + [LiClO_4] = 0{\cdot}61$M.

Titration of a fresh aqueous solution of the ester with alkali gives an end-point which is slightly greater than that calculated for half-hydrolysis. The methyl hydrogen selenate formed in this hydrolysis reacts fairly rapidly with hydroxide ion, and addition of an excess of alkali, followed by back-titration with acid, gives the end-point calculated for complete hydrolysis.

Hydrolysis of sodium methyl selenate is very slow in water, and autocatalysed. In perchloric acid the first-order rate constant, k_1', is approximately proportional to the acid concentration, and plots of log k_1' against log $[HClO_4]$ are linear, except at the extremes of the acidity scale, with slopes of 0·8 at 0° and 0·9 at 25° (Fig. 1). Plots of log k_1' against $-H_0$ (Hammett's acidity function [3a]) are smooth curves whose slopes decrease with

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[1] Kursanov and Kudryavtsev, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 3323; *Chem. Abs.*, 1957, **51**, 7814; Lauder, Wilson, and Zerner, *Austral. J. Chem.*, 1961, **14**, 41; Kaiser, Panar, and Westheimer, *J. Amer. Chem. Soc.*, in the press.

[2] (*a*) Burwell, *J. Amer. Chem. Soc.*, 1952, **74**, 1462; (*b*) Burstein and Lieberman, *ibid.*, 1958, **80**, 5235.

[3] (*a*) Long and Paul, *Chem. Rev.*, 1957, **57**, 935; (*b*) Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

increasing acidity. Addition of sodium chloride or bromide has little effect (Table 2). The solvent isotope effect, $k_{D_2O}/k_{H_2O} = 1{\cdot}36$, and the entropy and energy of activation, ΔS^* and E, are —23 e.u. and 17·6 kcal. mole^{-1}.

TABLE 2.

Hydrolysis of methyl hydrogen selenate.

(Dilatometry was used unless specified.)

(i) *Acid-catalysis.* Solvent = water.

(*a*) At 0°.

[HClO$_4$] (M)	0·10	0·53	1·92	1·98	3·00	3·91	4·91	5·92	6·85
$10^6k_1'$ (sec.$^{-1}$)	12·3 *	44·2 *	137	150	189	232	308	393	450

(*b*) At 25·1°.

[HClO$_4$] (M)	0·10					0·20	0·48	0·50	0·45	0·76
$10^5k_1'$ (sec.$^{-1}$)	16·7 *	17·3	17·8	22·7 †	15·6 ‡	29·7 *	61·3	59·4 *	62·7 §	93·5

[HClO$_4$] (M)	0·93	0·94	1·08	1·14	1·21	1·45	1·46	1·76	2·19
$10^5k_1'$ (sec.$^{-1}$)	111	112	126	133	140	162	155	195	245

(ii) *Variation of temperature.* Solvent = water. 0·1M-HClO$_4$.

Temp.	0°	11·7°	22·1°	25·1°			27·6°	29·9°	34·6°	34·8°	42·3°
$10^5k_1'$ (sec.$^{-1}$)	1·23 *	4·90 *	11·2	16·7 *	17·3	17·8	22·8	29·5 *	48·8	43·2 *	97·0

(iii) *Variation of solvent.* At 25·1°. 0·1M-HClO$_4$. Titrimetry.

Water (vol. %)	100	62	40	29	18	9·2
[H$_2$O] (mole %)	100	90·0	75·9	66·2	52·3	31·8
$10^5k_1'$ (sec.$^{-1}$)	17·3	19·3	31·8	48·9	122	205 **
,, ,, (calc.) ††	16·7	20·9	31·8	49·0	137	
,, ,, ,, ‡‡	12·5	16·9	32·6	49·0	115	

(iv) *Alkali.* Water at 0°. $k_2' \approx 2{\cdot}5$ l. mole^{-1} sec.$^{-1}$.

* Titrimetry. † D$_2$O. ‡ 0·4M-NaCl. § M-NaBr. ** 0·032M-MeO·SeO$_3$H catalyst. †† Calc. from equation 1a. ‡‡ Calc. from equation 1b.

Addition of dioxan speeds the acid hydrolysis (Table 2); this effect is in the opposite direction to that on the protonating power of the acid as measured by $-H_0$ (Hammett's acidity function),[3] but can be related approximately either to the mole fraction of water, m, or to the dielectric constant,[4] D:

$$10^3/k_1' = 11{\cdot}5m - 5{\cdot}6; \qquad (1a)$$

$$10^3/k_1' = 0{\cdot}138D - 0{\cdot}28. \qquad (1b)$$

It is not possible to assign the mechanism of the acid hydrolysis unambiguously from these observations. For hydrolysis of an initially neutral substrate the approximate proportionality of the rate with acid concentration rather than with h_0 suggests an A-2 mechanism,[3a] as would the values of the deuterium solvent isotope effect [5] and the entropy of activation.[6] But we have little evidence that these tests can be applied to hydrolysis of anionic substrates, and we therefore must compare the alkyl hydrogen selenates with the hydrogen sulphates.[2]

Acid-catalysed hydrolysis of alkyl sulphate ions occurs with sulphur–oxygen fission, and for various steroidal hydrogen sulphates reaction is enormously speeded by addition of inert diluents to the water.[2b] The rates of aromatic sulphonation and of esterification of sulphuric acid vary similarly with acidity, suggesting that they have a common mechanism.[3a,7] Sulphur trioxide is believed to be an active intermediate in aromatic

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[4] "The Physical Chemistry of Electrolyte Solutions," Harned and Owen, Reinhold Publ. Corp., New York, 1943, p. 118.

[5] Pritchard and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4162; cf. Bunton and Shiner, *ibid.*, 1961, **83**, 3207.

[6] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2632.

[7] Gold and Satchell, *J.*, 1956, 1635; Williams and Clark, *J.*, 1956, 1304; and refs. therein.

sulphonation, and by analogy in esterification, and therefore acid-hydrolysis (the reverse of esterification) should be written:

$$\mathrm{RO{\cdot}SO_3^- + H^+ \overset{\text{Fast}}{\rightleftharpoons} RO{\cdot}SO_3H \xrightarrow{\text{Slow}} ROH + SO_3}$$

(The fast and the slow step may be synchronous.)

This model explains the kinetic solvent effect upon the acid hydrolysis of steroidal hydrogen sulphates, because the initial state, a proton and an anion, should be destabilised, relatively to the transition state, by addition of an organic diluent.[2b] Ethers are particularly effective solvents because they can solvate the expelled sulphur trioxide. The entropies of activation are positive, as expected for a reaction in which the transition state is less solvated than the initial state, and depend on the solvent. In ethanol, $\Delta S^* = 11$ e.u., and $E = 29$ kcal. mole^{-1}.

Except for the similar solvent effects, the kinetic forms of the acid-hydrolysis of the alkyl hydrogen sulphates and selenates differ considerably, suggesting that the mechanisms are different. (1) The selenates are much the more reactive, *e.g.*, they are hydrolysed readily at 0° in water, whereas the sulphates react slowly at 100°.[2] (2) The entropy of activation is more negative and the energy of activation lower for the selenates.* If acid-hydrolysis of methyl hydrogen selenate involved merely elimination of (hypothetical) selenium trioxide there is no reason why the selenate should be very much more reactive than the sulphate, nor why the Arrhenius parameters should be so different. We therefore tentatively suggest an *A*-2 mechanism involving attack of water upon the selenium atom of methyl hydrogen selenate:

$$\mathrm{MeO{\cdot}SeO_3^- + H^+ \overset{\text{Fast}}{\rightleftharpoons} MeO{-\!\!-}\,\vdots\,SeO_3H \underset{\text{Slow}}{\overset{\mathrm{H_2O}}{\rightleftharpoons}} MeOH + H^+ + HSeO_4^-}$$

The Zucker–Hammett hypothesis has been used widely as a mechanistic test for acid-hydrolyses of neutral substrates.[3a] Fuller, Hughes, and Ingold have shown that an H_- scale, calculated from the protonation of picrate and sulphonate ions by hydrochloric or perchloric acid,[8] is parallel to the H_0 scale for acid concentration between 1·5 and 6M. An *A*-1 hydrolysis of the methyl selenate ion should therefore follow either of these acidity functions, because our initial state ($\mathrm{MeO{\cdot}SeO_3^-}$) should be very similar in structure to the indicator anion.

The Brönsted–Bjerrum equation for an *A*-2 hydrolysis is:

$$k_1' = k_0.\mathrm{a_{H^+}}.\mathrm{a_{H_2O}}f_{\mathrm{S^-}}/f^*_{\mathrm{HS,OH_2}} \tag{2}$$

(f is an activity coefficient, and $\mathrm{S^- = MeO{\cdot}SeO_3^-}$), and by approximations similar to those applied originally to *A*-2 hydrolyses of unchanged substrates,[3a] equation 2 becomes †

$$k_1' = k_0[\mathrm{H^+}];$$

and the kinetic form follows this equation reasonably well.

However, these approximations are of doubtful validity even for reactions of uncharged substrates,[3a,9] and they need testing on other reactions of known mechanism.

The negative value of the entropy of activation for methyl hydrogen selenate, and the value $k_{\mathrm{D_2O}}/k_{\mathrm{H_2O}}$ can also be used as permissive evidence for an *A*-2 mechanism; again by relying upon analogies with reactions of unchanged substrates or of alkyl sulphate ions. The increase of rate with addition of dioxan is to be expected because water will solvate the initial state more strongly than the transition state.

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* Some of the difference may be caused by differences in the solvents.

† The assumption that $f_{\mathrm{S^-}}f_{\mathrm{H_2O^+}}/f^*_{\mathrm{HS,OH_2}} \approx 1$ seems improbable, because the transition state is formally uncharged; however, it may have considerable polar character.

[8] Fuller, Hughes, and Ingold, unpublished results; Fuller, Thesis, London, 1961; cf. Boyd, *J. Amer. Chem. Soc.*, 1961, **83**, 4288.

[9] Whalley, *Trans. Faraday Soc.*, 1959, **55**, 798; Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, and accompanying papers.

Although water is very reactive towards methyl hydrogen selenate, halide ions are not (Table 2), and they have no appreciable salt effect. They behave very differently towards sulphite and sulphinate esters,[10] whose acid-hydrolyses are also accelerated by non-nucleophilic salts such as perchlorates. It is not known whether halide ions catalyse the hydrolysis of alkyl hydrogen sulphates, and dialkyl selinites are hydrolysed too rapidly for kinetic study,[11] but the present sparse evidence suggests that halide ions do not attack sulphur or selenium atoms in their higher oxidation states.

The rate of attack of hydroxide ion upon the selenium atom of the methyl selenate ion is only just measurable by conventional methods (Table 2), although it is an attack of one anion upon another. This fast attack upon selenium contrasts with the very slow saponification of alkyl sulphate ions, which takes place at *ca.* 100° with alkyl–oxygen fission.[2]

Hydrolysis of Dimethyl Selenate.—Addition of dioxan to water slows the first stage of hydrolysis, and speeds the second, and for solvents containing <50 mole % of water we measured the rate of hydrolysis of dimethyl selenate to methyl hydrogen selenate. The reaction in initially neutral dioxan-water (90·8 : 9·2 v/v) (see Experimental section) is autocatalysed. Perchloric acid speeds hydrolysis (Table 3), but a plot of the first-order rate constant, k_1, against acid concentration is convex (Fig. 2). (Methylselenic and perchloric acid are effective catalysts.) Added lithium perchlorate slows the reaction, and we think that perchloric acid has a negative salt effect which opposes the acid-catalysis and, for ionic strength of *ca.* 0·6M, k_1 is approximately proportional to acid concentration. Similar negative salt effects have been observed in acid-hydrolyses of alkyl trifluoroacetates [12] and aryl phosphate esters [13] in water or aqueous dioxan.

TABLE 3.

Hydrolysis of dimethyl selenate.

Perchloric acid unless specified. Reaction followed titrimetrically unless specified.

(i) *In dioxan–water* (90·8 : 9·2 v/v). At 25·1°.

[Acid] (M)	—	0·056	0·05		0·10		0·20		0·35	0·70
$10^6 k_1$ (sec.$^{-1}$)	13 *	*ca.* 47 *	41·2	37·5 †	68·7	38·6 ‡	92·6	55·8 §	107	136

(ii) *Variation of temperature.* 0·1M-$HClO_4$.

Temp.	25·1°	30·0°	35·6°
$10^6 k_1$ (sec.$^{-1}$)	68·7	88·2	127

(iii) *Variation of solvent.* At 25·1°. 0·1M-$HClO_4$.

Water (vol. %)	3·9	9·2	16·7
[H_2O] (mole %)	15·9	31·3	48·8
$10^6 k_1$ (sec.$^{-1}$)	38·8	68·7	182

* Methyl hydrogen selenate and selenic acid are the catalysts for these reactions which were followed conductimetrically. † 0·24M-$LiClO_4$. ‡ 0·51M-$LiClO_4$. § 0·41M-$LiClO_4$.

The energy of activation is *ca.* 11 kcal. mole^{-1} and the Arrhenius non-exponential term is *ca.* 10^5 l. mole^{-1} sec.$^{-1}$, corresponding to $\Delta S^* \approx -50$ e.u. These values are approximate, because the temperature range was small and reaction is a composite of a spontaneous and an acid-catalysed hydrolysis; but the entropy of activation is much more negative, and the energy much lower, than for the acid-hydrolysis of either the methyl selenate ion (p. 3132) or dimethyl sulphate.[14] Negative values of ΔS^*, and low energies of activation, are also found in hydrolyses of alkyl trifluoroacetates [12] and aryl phosphates.[13] For 0·1M-perchloric acid, addition of water speeds hydrolysis very markedly (Table 3), in sharp contrast to the solvent effect on hydrolysis of the anion. It is tempting

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[10] Bunton, de la Mare, and Tillett, *J.*, 1959, 1766; Tillett, *J.*, 1960, 5138; Bunton and Hendy, *J.*, 1962, 2562.

[11] Bunton and Hendy, following paper.

[12] Bunton and Hadwick, *J.*, 1958, 3248; 1961, 943.

[13] Vernon, *Chem. Soc. Special Publ.*, 1957, No. 8, p. 17.

[14] Robertson, Heppolette, and Scott, *Canad. J. Chem.*, 1959, **37**, 803, and refs. therein.

to suppose that low Arrhenius parameters, negative salt effects, and a strong rate-dependence on the water content of the solvent are characteristic of reactions in which a large number of water molecules cluster round the reaction centre in the transition state.

The hydrolysis of dimethyl selenate is very different from those of dimethyl sulphate, or a methyl sulphonate, in which a water molecule attacks carbon. We assume that both the spontaneous and the acid-hydrolyses involve bimolecular attack by water upon selenium, otherwise there is no reason why the selenate should be much more reactive than the sulphate (cf. p. 3133). Acid-catalysed hydrolysis of the ester of a strong acid is unusual, although decompositions and rearrangements of some alkyl halides and sulphonates in aprotic solvents are acid-catalysed.[15]

Reasonable hydrolysis mechanisms are:

Neutral hydrolysis

$$\mathrm{MeO{\cdot}SeO_2 \vdots\!-\!OMe + H_2O \longrightarrow MeO{\cdot}SeO_3^- + MeOH + H^+}$$

Acid hydrolysis

$$\mathrm{H^+ + (MeO)_2SeO_2 \xrightleftharpoons{\textbf{Fast}} (MeO)_2SeO_2H^+}$$

$$\mathrm{MeOSeO_2H^+ \vdots\!-\!OMe + H_2O \longrightarrow MeOSeO_3^- + MeOH + 2H^+}$$

The position of the proton, and the timing of the covalency changes, are uncertain.

In accord with those differences between the hydrolyses of dimethyl sulphate and selenate, we find that the selenate is less effective at methylating the phenoxide ion (Experimental section).

This greater reactivity of these selenium esters to nucleophiles, when compared with the corresponding sulphur esters, is to be expected, and because telluric acid exists as H_6TeO_6 [16] we should expect the corresponding tellurates to be even more reactive. The halogen oxy-acids provide many examples of this increasing electrophilicity with increasing atomic number.[17]

Esterification of Selenic Acid.—Selenic acid is esterified by primary and secondary alcohols. The equilibrium constants, K, calculated for formation of the alkyl hydrogen selenate, are in Table 4. They are very small for tertiary alcohols; selenic acid and sulphuric acid behave similarly.[18] (The experiments with tertiary alcohols may be ambiguous, either because the acid dehydrates the alcohol or because the t-alkyl ester is so unstable that it is titrated by alkali as if it were the free acid.)

TABLE 4.

Esterification of selenic acid at 25°.

R:	Me	Et	Pr^i	$Ph{\cdot}CH_2$	Bu^t	CMe_2Et
10^2K:	7	14	8	5	*ca.* 0·01	*ca.* 0·01

EXPERIMENTAL

Materials.—Dimethyl selenate was prepared from dried, powdered silver selenate and refluxing methyl iodide. After 6—8 hr. the filtrate was shaken with mercury, the solution concentrated, and the ester purified by molecular distillation (50°/10^{-3} mm.; cf. ref. 19). The manipulations were made in a dry-box where possible. The ester is initially pale yellow, but becomes red with time, probably owing to the formation of selenium (Found: C, 14·3; H, 3·5; Se, 45·1. Calc. for $C_2H_6O_4Se$: C, 13·9; H, 3·5; Se, 45·5%). For various preparations the molecular weight, determined by saponification, ranged from 173 to 176 (calc., 173), and n^{25} from 1·4420 to 1·4430 [lit.,[19] n^{19} = 1·4410—1·4547, n^{25} = 1·4316 (undistilled)].

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[15] Bartlett and Pöckel, *J. Amer. Chem. Soc.*, 1938, **60**, 1585; Winstein, Smith, and Fainberg, *ibid.*, 1961, **83**, 618.

[16] Sidgwick, " Chemical Elements and their Compounds," Oxford Univ. Press, Oxford, 1950, p. 981.

[17] Hoering, Butler, and McDonald, *J. Amer. Chem. Soc.*, 1956, **78**, 4829.

[18] Suter, " The Organic Chemistry of Sulphur," Wiley, New York, 1945, p. 4.

[19] Meyer and Wagner, *Chem. Ber.*, 1922, **55**, 1216; Meyer and Hinke, *Z. anorg. Chem.*, 1932, **204**, 29; Strecker and Daniel, *Annalen*, 1928, **462**, 186.

The infrared spectrum of the liquid had a strong band at 6·9, and prominent broad doublets at 10—10·6 and 15·3—15·9 μ characteristic of Se=O and Se–O–C bonds, respectively,[20] and small peaks at 5·2, 6·3, 7·2, 7·9, 8·3, 8·6, 9·2, 11·5, and 12·0 μ.

The ester was stored at −80°. This precaution seems to be unnecessary, because a sample kept in a desiccator for 10 months at room temperature had n^{25} 1·4432 and an unchanged infrared spectrum.

Bond Fission.—The procedure is described in ref. 10.

Kinetics.—*Hydrolysis of the methyl selenate ion.* Rapid titration of a solution of dimethyl selenate at 0° with sodium hydroxide gives an end-point which is slightly greater than half that calculated for complete reaction (*ca.* 55%); there is then a comparatively slow reaction with added alkali, until 2 equiv. of it are consumed.

Addition of dimethyl selenate to conductivity water at 0° gives an immediate increase in conductivity to the value expected for a monobasic acid (Table 5). There is then a slow increase in conductivity to the value expected for selenic acid. The conductivity readings became erratic after the solution had been several days in the cell; the solution was therefore removed and the cell cleaned. We think that deposition of small amounts of selenium upon the bright platinum electrodes caused this trouble.

TABLE 5.

Conductivity of methyl hydrogen selenate in water at 0°.

10^4 [Ester] (M)	21·7		54·2		
Time (hr.)	0	1	0	36	5000
Λ (ohm^{-1} mole^{-1} l.) *	240 (415)	257	240 (450)	344	454

* Calc. in terms of moles of Me_2SeO_4 added. Value for selenic acid in parentheses. For freshly made solutions of methyl hydrogen selenate at 0°, $\Lambda \approx 245 - 130\sqrt{c}$ (c is ester concn. in mole l.$^{-1}$).

Addition of dimethyl selenate to aqueous silver nitrate at 0° gave an immediate yellow-white precipitate, although in dioxan–water (90·8 : 9·2 v/v) there was an opalescence followed only slowly (>15 min.) by formation of a yellow-white precipitate. In either water or aqueous dioxan selenic acid gave an immediate precipitate.

Therefore the ester is immediately hydrolysed in water to methyl hydrogen selenate; and our kinetic solutions were prepared by neutralising these aqueous solutions quickly with sodium hydroxide solution. Sodium methyl selenate is reasonably stable in water, but fresh solutions were always used, and reagents, or co-solvent, were added to them to give the kinetic solutions. The spontaneous hydrolysis of the methyl selenate ion is slow in water, $10^7 k_1' \approx 2$ sec.$^{-1}$ at 20° (from variation of pH with time).

The acid-catalysed hydrolysis was followed titrimetrically (for low acid concentrations) with Bromothymol Blue as indicator, or by dilatometry, which could be used over a wide range of acid concentration. The contraction during reaction becomes small at high acid concentrations, probably because the hydrogen selenate ion is a weak acid. The same problem arises in acid hydrolyses of alkyl trifluoroacetates.[12]

The second-order rate constant, k_2', for alkaline hydrolysis of the methyl selenate ion was obtained by mixing an aqueous solution of sodium methyl selenate with an equivalent solution of sodium hydroxide at 0°. A known excess of standard hydrochloric acid was added after a few seconds, and the solution was back-titrated with sodium hydroxide. Four experiments gave $k_2' = 22$, 23, 33, and 22 l. mole^{-1} sec.$^{-1}$.

Hydrolysis of Dimethyl Selenate.—Hydrolysis in aqueous dioxan was followed (1) conductimetrically, or (2) titrimetrically.

(1) When dimethyl selenate was dissolved in dioxan–water (90·8 : 9·2 v/v) at 25·1°, the conductivity increased slowly to that of an equivalent solution of methyl hydrogen selenate (prepared by dissolving the ester in water and adding dioxan to it). The hydrogen selenate ion is a weak acid and therefore the conductivities of solutions of selenic acid and methyl hydrogen selenate should be similar, and in dioxan–water (90·8 : 9·2 v/v) at 25·1°, the specific conductivities, $10^5\kappa$, are:

10^2 [$MeO{\cdot}SeO_3H$] (M)	2·32	3·48
$10^5\kappa$ (ohm^{-1})	0·90 (0·89)	1·37 (1·34)

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[20] Paetzold and Simon, *Z. anorg. Chem.*, 1960, **303**, 53.

(The values in parentheses are for equimolar solutions of H_2SeO_4.) The reaction, which can be followed conductimetrically, is autocatalysed and from the slopes of a plot of log $[Me_2SeO_4]$ against time we estimate instantaneous values of k_1. These are initially constant, but then increase owing to acid autocatalysis, and for a given concentration of selenic acid are similar to those observed in perchloric acid (Table 3, and Fig. 2).

For the hydrolysis of dimethyl selenate in initially neutral dioxan–water (90·8 : 9·2 v/v) at 25·1°, $[Me_2SeO_4]$ was calculated from the acid concentration. A plot of log $[Me_2SO_4]$ against time was linear for 120 min. (8% of reaction); then the curve steepened, and the slope at 16·3 hr. gave $10^6k_1 \approx 47$ sec.$^{-1}$.

Time (hr.)	2·75	16·3	18·2	21·4
$2 + \log [Me_2SeO_4]$	0·793	0·301	0·152	0·033

(2) The titrimetric method requires that in acidic aqueous–dioxan the second stage of hydrolysis, that of the methyl selenate ion, should be faster than the first, but in water much slower. These requirements are met if the dioxan content of the solvent is greater than 85 vol. % and $[H^+] \geqslant 0·03$M. Portions (5 c.c.) of the kinetic solution (aqueous dioxan of low water content) were added to water (20 c.c.). Hydrolysis of unchanged dimethyl selenate was then very rapid, but that of methyl hydrogen selenate was very slow. The total acid was titrated with aqueous sodium hydroxide to Bromothymol Blue. If a is the initial ester concentration, and $[H^+]$ that of the catalysing acid, then at $t = 0$ the equivalents of sodium hydroxide consumed will be $(a + [H^+])$ and at time t, when x moles of dimethyl selenate have been hydrolysed, the alkali consumed will be $\{[H^+] + (a - x) + 2x\}$, and at complete reaction $([H^+] + 2a)$.

Methylation.—Reaction between dimethyl selenate (*ca.* 0·8 g.) and a 3-fold excess of sodium phenoxide in dry methanol gave after 12 hr. at 25° a 20% yield of anisole (identified by gas-liquid chromatography and infrared spectrum).

Esterification of Selenic Acid.—Selenic acid (*ca.* 1·5 mole) was dissolved in a 50-fold molar excess of alcohol at 25·1°, and after 3 days the solution was titrated with standard sodium hydroxide (to determine $2[H_2SeO_4] + [R{\cdot}SeO_4H]$). Excess alkali was then added to hydrolyse the sodium alkyl selenate, and the final excess back-titrated with standard hydrochloric acid. The equilibrium constant, $K = [RO{\cdot}SeO_3H][H_2O]/[ROH][H_2SeO_4]$, was calculated on the assumption that no dialkyl selenate was formed.

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