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STUDIES ON SELENATES

II. THERMAL DECOMPOSITION OF HEAVIER RARE-EARTH SELENATE HYDRATES

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ABSTRACT

Thermogravimetry, differential thermal analysis and differential thermogravimetry have been used to study the decomposition of hydrated selenates of heavier rare-earths and yttrium. Based on the results obtained, mechanisms of dehydration-decomposition have been proposed. Dehydration temperatures of the hydrated selenates show a gradual decrease with order of rare-earth elements.

INTRODUCTION

Several investigations have been carried out on the thermal behaviour of rare-earth sulphate hydrates[1–3]. In contrast the selenates of rare-earth elements have received relatively little attention. Only recently few reports have been published on the thermal dehydration-decomposition of rare-earth selenate hydrates. Giolito and Giesbrecht[4] have reported the thermal decomposition of rare-earth selenates using TG data. Almost simultaneously Belik and Serebrennikov[5] studied the thermal stability of some common hydrates of rare-earth selenates. These investigations on selenates have been primarily concerned with steps of decomposition and with their conversion into oxides, rather than with the steps of dehydration. The present communication, which is a part of a comprehensive study[6–9] of selenates, deals with the dehydration-decomposition of crystallohydrates of heavier rare-earth selenates including yttrium.

EXPERIMENTAL

The rare-earth selenates in the present investigation were synthesised by treating the respective rare-earth hydroxides with selenic acid. An excess of hydroxide was always maintained in solution. The solution was filtered, followed by crystallisation in vacuum over P_2O_5. All the synthesised selenates were chemically analysed on metal and selenate. The metal contents were determined by complexometric back titrations. Selenate was estimated after eluting the aqueous salt solution through a cation exchanger Dowex 50 X 8, followed by simple acid–base titration of the effluent electrolyte.

The lower hydrates, anhydrides and intermediate products isolated by static thermal decomposition were also chemically analysed. These products being sparingly soluble, a little dilute hydrochloric acid was used to prepare their solutions. These were analysed on metal components complexometrically as above. However, the selenate contents were determined gravimetrically by precipitating them as barium selenate from the solutions. Table 1 summarises the results of the chemical analysis of synthesised selenate hydrates, isothermally isolated lower hydrate, anhydrides and intermediate products. This table also includes the percentage of water obtained during thermal analysis. The course of decomposition of selenates was investigated by thermogravimetric (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) as described previously[6].

TABLE 1

ANALYTICAL AND THERMOANALYTICAL RESULTS

n.a. = not analysed.

Compound	*Analytical results*					
	Metal (%)		*Selenate (%)*		*Water (%)*	
	Calc.	*Anal.*	*Calc.*	*Anal.*	*Calc.*	*Anal.*
$Tb_2(SeO_4)_3 \cdot 8H_2O$	35.69	35.55	48.14	48.11	16.16	16.20
$Tb_2(SeO_4)_3$	42.56	42.49	57.43	57.35	—	—
$Tb_2O_2(SeO_3)$	66.66	66.69	n.a.		—	—
$Dy_2(SeO_4)_3 \cdot 8H_2O$	36.19	36.23	47.76	47.70	16.03	16.38
$Dy_2(SeO_4)_3$	43.11	42.97	56.89	56.94	—	—
$Dy_2O_2(SeO_3)$	67.15	67.07	n.a.		—	—
$Ho_2(SeO_4)_3 \cdot 8H_2O$	36.54	36.46	47.50	47.31	15.96	15.72
$Ho_2(SeO_4)_3$	43.48	43.51	56.52	56.59	—	—
$Ho_2O_2(SeO_3)$	67.48	67.40	n.a.		—	—
$Er_2(SeO_4)_3 \cdot 8H_2O$	36.86	36.63	47.26	47.74	15.86	15.03
$Er_2(SeO_4)_3$	43.76	43.44	56.18	55.99	—	—
$Er_2O_2(SeO_3)$	67.79	67.79	n.a.		—	—
$Tm_2(SeO_4)_3 \cdot 8H_2O$	37.09	37.07	47.08	46.92	15.81	15.26
$Tm_2(SeO_4)_3$	44.06	44.18	55.93	55.89	—	—
$Tm_2O_2(SeO_3)$	68.00	68.10	n.a.		—	—
$Yb_2(SeO_4)_3 \cdot 8H_2O$	37.66	37.73	46.66	46.51	14.66	14.86
$Yb_2(SeO_4)_3$	44.66	44.72	55.34	55.42	—	—
$Yb_2O_2(SeO_3)$	68.52	68.58	n.a.		—	—
$Lu_2(SeO_4)_3 \cdot 12H_2O$	35.18	35.01	43.11	42.92	21.72	21.09
$Lu_2(SeO_4)_3$	44.93	44.97	55.06	54.95	—	—
$Lu_2O_2(SeO_3)$	68.77	68.71	n.a.		—	—
$Y_2(SeO_4)_3 \cdot 8H_2O$	23.68	23.68	57.13	57.44	19.19	20.85
$Y_2(SeO_4)_3 \cdot 7H_2O$	24.31	24.64	58.60	58.95	17.19	16.41[a]
$Y_2(SeO_4)_3$	29.36	30.20	70.78	70.25	—	—
$Y_2O_2(SeO_3)$	52.82	52.17	n.a.		—	—

[a] % of water determined by difference.

RESULTS AND DISCUSSION

Simultaneous TG, DTA and DTG curves were obtained for the selenate hydrates of Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. The general trend of thermoanalytical curves of Tb–Lu selenates is closely similar to each other, except for Ho and Lu, where very unstable intermediate hydrates are noticeable. $Y_2(SeO_4)_3 \cdot 8H_2O$ exhibits a definite intermediate hydrate. Figs. 1–5 represent the thermoanalytical curves for $Dy_2(SeO_4)_3 \cdot 8H_2O$, $Ho_2(SeO_4)_3 \cdot 8H_2O$, $Er_2(SeO_4)_3 \cdot 8H_2O$, $Lu_2(SeO_4)_3 \cdot 12H_2O$ and $Y_2(SeO_4)_3 \cdot 8H_2O$, respectively.

It is evident from the thermoanalytical curves obtained that the rare-earth selenate hydrates lose their stability between 100–120°C. Holmium and yttrium are the exceptional cases, where the stability is lost just above the room temperature. Further rise in temperature brings about the one step dehydration of Tb, Dy and Er–Yb selenate hydrates. Thus, no intermediate hydrate is identified as in the case

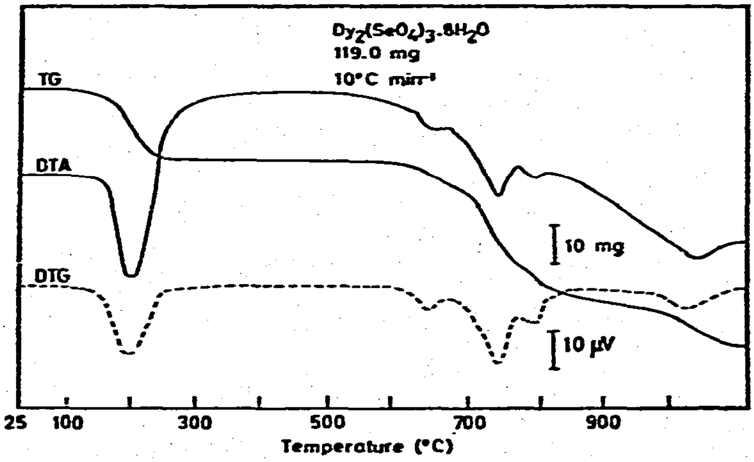


Fig. 1. Simultaneous TG–DTA–DTG of $Dy_2(SeO_4)_3 \cdot 8H_2O$.

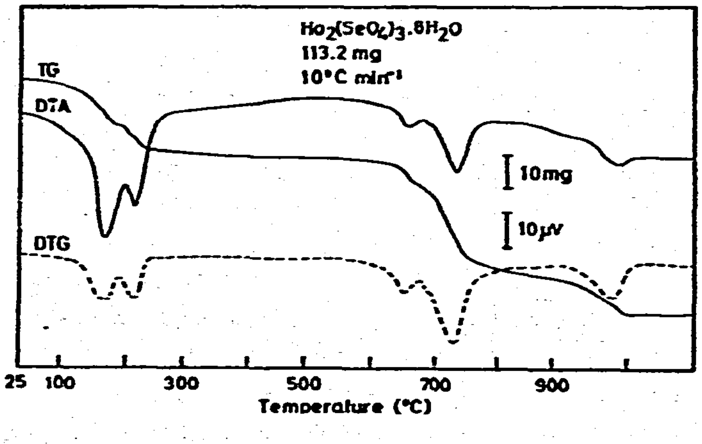


Fig. 2. Simultaneous TG–DTA–DTG of $Ho_2(SeO_4)_3 \cdot 8H_2O$.

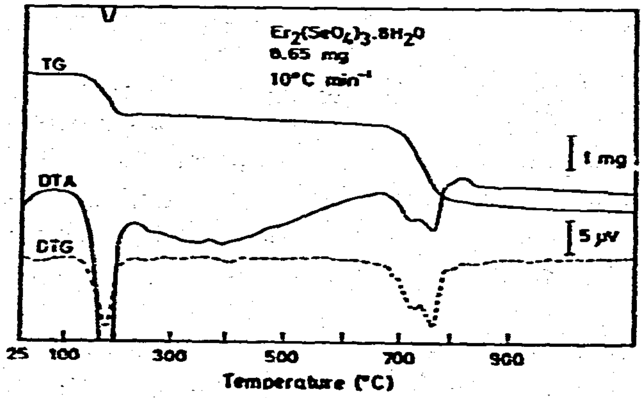


Fig. 3. Simultaneous TG–DTA–DTG of $Er_2(SeO_4)_3 \cdot 8H_2O$.

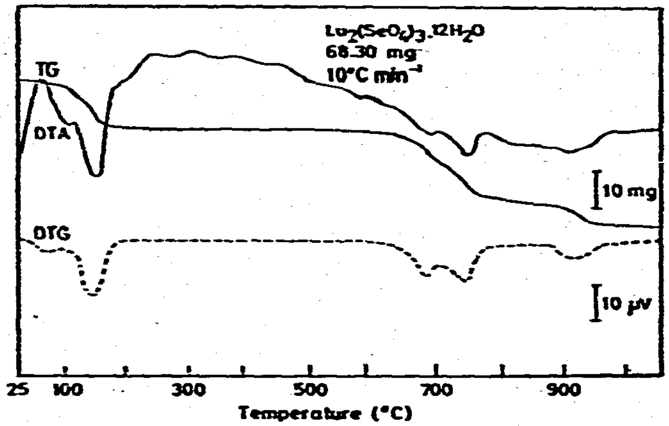


Fig. 4. Simultaneous TG–DTA–DTG of $Lu_2(SeO_4)_3 \cdot 12H_2O$.

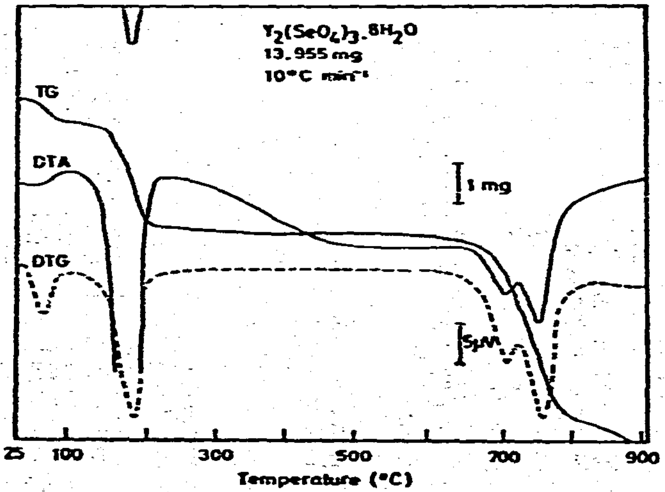


Fig. 5. Simultaneous TG–DTA–DTG of $Y_2(SeO_4)_3 \cdot 8H_2O$.

of rare-earth sulphates[3]. Thermogravimetric curves of Ho and Lu selenates, however, show the existence of a very unstable intermediate hydrate as seen from the breaks on slope of the curves. The break at 180 and 110°C corresponds to the loss of six moles and to two moles of water in holmium and lutetium selenate, respectively. Yttrium selenate octahydrate shows a notable deviation from the general trend of dehydration. It loses seven molecules of water in a single step at 70°C, forming a monohydrate, indicating that the remaining molecule of water is bonded in a different way. The last molecule is lost at 190°C.

In general the temperature at which the reaction

$$M_2(SeO_4)_3 \cdot nH_2O \rightarrow M_2(SeO_4)_3 + nH_2O$$

becomes noticeable ranges from 190 to 285°C. The trend appears to be that this temperature decreases gradually in order of rare-earth elements, indicating the ease of deaquation with decreasing ionic radii of the metal ion. Figure 6 exhibits a regular decrease in TG temperature in the order of increasing atomic number, which is in accordance with lanthanide contraction. Endothermic activities associated with the above dehydrations are detected in DTA curves of temperatures ranging between 160 and 190°C.

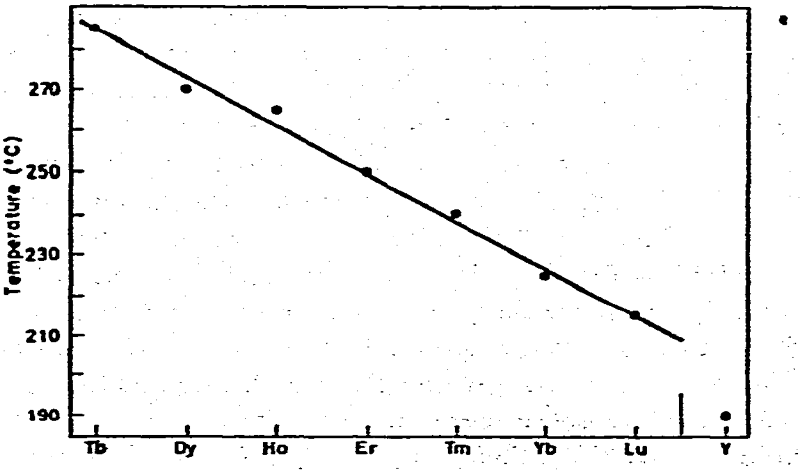


Fig. 6. The dehydration temperatures of rare-earth selenates.

The course of dehydration of selenate hydrates as determined by DTA and TG is summarised in Table 2, in which the second column reports the temperature of maxima in DTA curves and the fourth, the temperature of weight level in TG curves.

The horizontal of the anhydrides persists over a long range of temperature, exhibiting their appreciable thermal stability. The temperatures at which the $M_2(SeO_4)_3$ stage becomes susceptible, range between 600 to 830°C. However, these temperatures do not have any regularity as might be expected. Further elevation in temperature reduces the anhydride to selenite and subsequently to oxyselenite with sublimation of selenium dioxide.

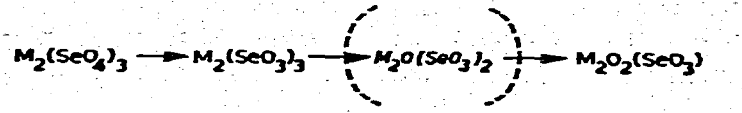
TABLE 2

DEHYDRATION OF HYDRATED SELENATES

	DTA effects		*Temp. on TG curves* (°C)	*Interpretation*
	Temp. (°C)	*Nature*		
$Tb_2(SeO_4)_3 \cdot 8H_2O$	190	large endotherm	285	loss of $8H_2O$
$Dy_2(SeO_4)_3 \cdot 8H_2O$	190	large endotherm	270	loss of $8H_2O$
$Ho_2(SeO_4)_3 \cdot 8H_2O$	170	medium endotherm	180	loss of $6H_2O$
	210	small endotherm	265	loss of $2H_2O$
$Er_2(SeO_4)_3 \cdot 8H_2O$	180	medium endotherm	250	loss of $8H_2O$
$Tm_2(SeO_4)_3 \cdot 8H_2O$	180	large endotherm	240	loss of $8H_2O$
$Yb_2(SeO_4)_3 \cdot 8H_2O$	165	large endotherm	225	loss of $8H_2O$
$Lu_2(SeO_4)_3 \cdot 12H_2O$	105	small endotherm	110	loss of $2H_2O$
	160	medium endotherm	215	loss of $10H_2O$
$Y_2(SeO_4)_3 \cdot 8H_2O$	55	small endotherm	70	loss of $7H_2O$
	170	large endotherm	190	loss of $1H_2O$

The decomposition of the anhydride to oxyselenite in the present investigation clearly indicates transient existence of intermediates as evident from slight inflexion points instead of horizontal levels in TG curves. For terbium and dysprosium selenate anhydrides (Fig. 1) three DTG peaks corresponding to three mass losses are observed. The prominent break on the TG curves at 670 and at 660°C indicates the formation of selenite of Tb and Dy, respectively. Above these temperatures, subsequent decomposition of the selenite results into a loss of one mole of selenium dioxide, corresponding to the formation of (*mono*)oxyselenite, $M_2O(SeO_3)_2$ of these two elements. The break on the TG curves at 750 and 760°C for Tb and Dy, respectively, accounts for the above decomposition. Further elevation in temperature brings about a loss of one mole of selenium dioxide from (*mono*)oxyselenite. This loss at 820 and at 830°C for Tb and Dy is attributable to the formation of (*di*)oxyselenite, $M_2O_2(SeO_3)$, respectively. This stage is quite stable as seen from the moderate horizontals on the TG curves. DTA curves for terbium and dysprosium selenates are almost identical to those observed for lanthanum selenate[9] and three peaks in each case undoubtedly correspond to a similar type of decomposition reaction.

Decomposition of holmium selenate anhydride probably involves all the three stages described above, although these are not so apparent on corresponding TG curves. However, a shoulder peak at 695°C in both DTA and DTG is seen (Fig. 2) besides two peaks at 675 and 790°C. This can be the consequence of transient existence of holmium (*mono*)oxyselenite and its subsequent decomposition to (*di*)oxyselenite. Holmium (*di*)oxyselenite, $Ho_2O_2(SeO_3)$ is formed at 790°C. It is noteworthy here, that (*mono*)oxyselenite is not noticed during the decomposition of Er–Lu and Y selenate anhydrides (Figs. 3–5). The decomposition of anhydride to (*di*)oxyselenite may be generalised as follows:



Formation of selenites and (*di*)oxyselenites of Ho–Lu and Y takes place at the temperature range 675–725°C and 760–830°C, respectively. However, no systematic variation is noticed for these temperatures.

The sequence of decomposition of the anhydrous selenates as determined by DTA and TG is summarised in Table 3, in which the significance of the temperatures is as described above for Table 2.

TABLE 3

DECOMPOSITION OF ANHYDROUS SELENATES

	DTA effects		*Temp. on TG curves* (°C)	*Interpretation*
	Temp. (°C)	*Nature*		
$Tb_2(SeO_4)_3$	650	small endotherm	670	a
	725	medium endotherm	750	b
	800	small endotherm	820	c
	1000	very small endotherm	>1000	d
$Dy_2(SeO_4)_3$	640	very small endotherm	660	a
	735	medium endotherm	760	b
	790	small endotherm	830	c
	1000	very small endotherm	>1000	d
$Ho_2(SeO_4)_3$	665	small endotherm	675	a
	695	(shoulder) endotherm	695	b
	740	medium endotherm	790	c
	1000	small endotherm	>1000	d
$Er_2(SeO_4)_3$	705	very small endotherm	720	a
	740	small endotherm	800	c
$Tm_2(SeO_4)_3$	660	very small endotherm	690	a
	735	medium endotherm	830	c
	980	very small endotherm	1000	d
$Yb_2(SeO_4)_3$	690	very small endotherm	700	a
	720	very small endotherm	755	c
$Lu_2(SeO_4)_3$	685	medium endotherm	700	a
	740	medium endotherm	760	c
	910	very small endotherm	1000	d
$Y_2(SeO_4)_3$	695	small endotherm	725	a
	735	medium endotherm	765	c

a = formation of selenite, b = formation of (*mono*)oxyselenite, c = formation of (*di*)oxyselenite, d = formation of sesquioxide.

The decomposition of (*di*)oxyselenites to corresponding metal oxides (with a loss of one mole of selenium dioxide)

$$M_2O_2(SeO_3) \rightarrow M_2O_3$$

takes place at temperature above 1000°C. The metal oxides could be obtained for Tb, Dy, Ho, Tm and Lu. This could not be achieved in the remaining cases as a low temperatures (800°C) furnace was used. Decomposition of (*di*)oxyselenite to metal oxide involves a very minor endothermal activity in DTA curves. Table 3 summarises the DTA and TG data for this final stage of decomposition.

CONCLUDING REMARKS

The present thermal investigations on heavier rare-earth selenate hydrates have revealed an interesting dehydration–decomposition mechanism. It is seen that the temperature of complete deaquation shows (Fig. 6) a regular fall with increasing order of rare-earth elements. It is also evident that the stability of (*mono*)oxyselenite decreases in the same order, under the experimental conditions followed in this work. Moreover, decomposition temperatures of anhydrides do not show systematic regularity as in the case of corresponding sulphates[3]. Finally the decomposition proceeds to the formation of sesquioxide through (*di*)oxyselenite. This decomposition scheme is in complete agreement with reports on scandium[10] and lanthanum[9] selenate pentahydrate.

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