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Note

THERMAL DECOMPOSITION OF MAGNESIUM AND CALCIUM SELENATES

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The preparation and description of some properties of magnesium selenate hepta- and hexahydrates and calcium selenate dihydrate [1] have been reported previously. There are also references to the isothermal dehydration [2,3] and the thermodecomposition [4] of magnesium selenate hexahydrate. No reference was found in the literature about the thermal decomposition of calcium selenate hemipentahydrate.

EXPERIMENTAL

Magnesium and calcium selenates were prepared by adding a 25% (v/v) water solution of recently prepared selenic acid [5] to hot suspensions in water of the corresponding metal carbonate. The final neutralization was carried out in a cold solution in the absence of CO_2. Both solutions were allowed to evaporate to near dryness in a desiccator over anhydrous calcium chloride at ambient temperature and pressure. The resulting crystals were removed from the mother liquor and kept in another desiccator over anhydrous calcium chloride until constant weight was attained. After an initial rapid weight loss the magnesium selenate hydrate sample continued to lose weight very slowly, and it was necessary to keep it in the desiccator for 18 months before it attained constant weight.

Magnesium and calcium ions were determined by complexometric titrations with EDTA standard solution, using Erio T and Calcon as indicators respectively [6]. The water of crystallization and the selenium contents were

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determined from the thermogravimetric (TG) curve. The TG and differential thermal analysis (DTA) curves were obtained as described previously [7].

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared, having the formulae: $MgSeO_4 \cdot 6H_2O$ (recently prepared), $MgSeO_4 \cdot 5H_2O$ (obtained after drying for 18 months in a desiccator over anhydrous calcium chloride), and $CaSeO_4 \cdot 2.5H_2O$. The TG curves of these compounds are presented in Fig. 1.

As seen from the TG curves in Fig. 1(a,b) the thermodecomposition of the hexa- and pentahydrates starts with dehydration occurring in four steps between 60 and 350 °C. Both compounds differ only in the first step: the hexahydrate loses 1.5 H_2O and the pentahydrate 0.5 H_2O. The subsequent three steps correspond to the losses of 3, 1.5 and 0.5 H_2O. Both TG curves show the successive formation of three intermediate compounds: heminonahydrate, $MgSeO_4 \cdot 4.5H_2O$; and hemihydrate, $MgSeO_4 \cdot 0.5H_2O$. The anhydrous salt is stable up to 600 °C and undergoes final thermodecomposition between 600 and 750 °C, giving magnesium oxide as the residue.

The DTA curve of magnesium selenate pentahydrate [Fig. 2a] shows four endothermic peaks (110, 150, 280 and 360 °C) corresponding to the water losses observed in the TG curve of Fig. 1a. The overlapped peaks at 705, 730 and 780 °C are probably due to the reduction of the anhydrous magnesium selenate to magnesium selenite (705 °C), which rapidly undergoes thermodecomposition to magnesium oxide.

The TG curves [Fig. 1(a,b)] and the DTA curve [Fig. 2a] allow the suggestion that the reactions taking place during the thermal decomposition of magnesium selenate hexa- and pentahydrate can be summarized by the following steps

$$\begin{tikzcd}
 & & MgSeO_4 \cdot 6H_2O + MgSeO_4 \cdot 5H_2O \arrow[r] & MgSeO_4 \cdot 4.5H_2O \arrow[d] \\
MgO & (MgSeO_3) \arrow[l] & MgSeO_4 \cdot 0.5H_2O \arrow[l] & MgSeO_4 \cdot 1.5H_2O \arrow[l]
\end{tikzcd}$$

TABLE 1

Analytical and thermoanalytical (TG) data

Compound	Analytical results					
	Mg or Ca (%)		Se (%)		H_2O (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$MgSeO_4 \cdot 6H_2O$	8.83	8.51	28.67	28.12	39.26	39.36
$MgSeO_4 \cdot 5H_2O$	9.44	9.85	30.68	31.13	35.01	35.00
$CaSeO_4 \cdot 2.5H_2O$	17.57	17.45	34.62	35.58	19.75	19.77

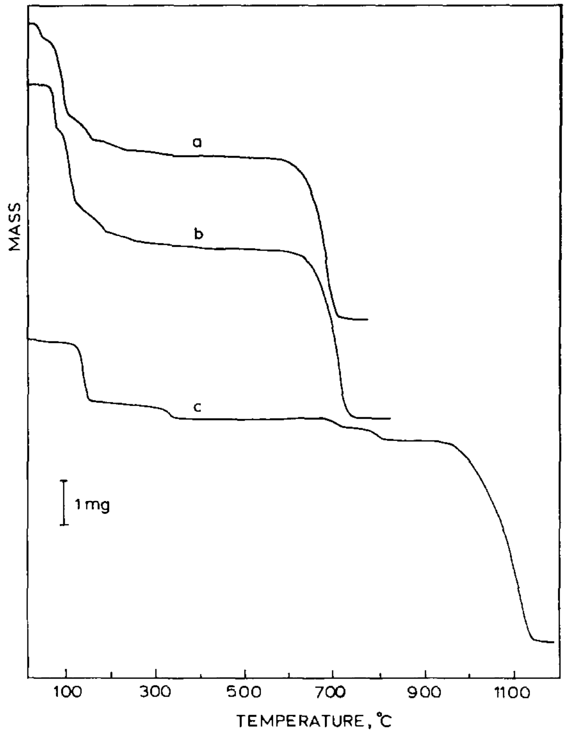

Fig. 1. TG curves of magnesium and calcium selenate hydrates (heating rate 6.25 °C min^{-1}). a, $MgSeO_4 \cdot 5H_2O$ (8.00 mg); b, $MgSeO_4 \cdot 6H_2O$ (9.02 mg); c, $CaSeO_4 \cdot 2.5H_2O$ (8.60 mg).

This thermodecomposition mechanism agrees with that reported by Nabar and Paralkar [4] only with regard to the thermal decomposition of the anhydrous salt. With respect to the dehydration mechanism, the formation of the mono- and tetrahydrates as described by Selivanova et al. [2], the formation of the dihydrate reported by Klein [3], and the penta- and trihydrate reported by Nabar and Paralkar [4] were not observed in the present study. The heminonahydrate and hemitrihydrate described in the present report were also obtained by Klein [3] and Mellor [1].

The first and the second mass losses observed in the TG curve of calcium selenate hemipentahydrate [$CaSeO_4 \cdot 2.5H_2O$, Fig. 1c], between 120 and 170 ° and 1250 and 350 °C, are due to dehydration and correspond to the loss of 2 and 0.5 H_2O respectively. The anhydrous salt is stable up to 680 °C. The two equal small mass losses occurring between 680 and 820 °C are probably due to the reduction of the selenate to selenite ion, and occur in two steps. The first mass loss (680–730 °C) suggests partial reduction with the formation of an intermediate compound ($CaSeO_4 \cdot CaSeO_3$) and the second (750–820 °C), corresponds to the total reduction of that intermediate to calcium selenite.

Three samples of calcium selenate pentahydrate were heated to 550, 740 and 840 °C at a rate of 10 °C min^{-1} in small platinum crucibles suspended

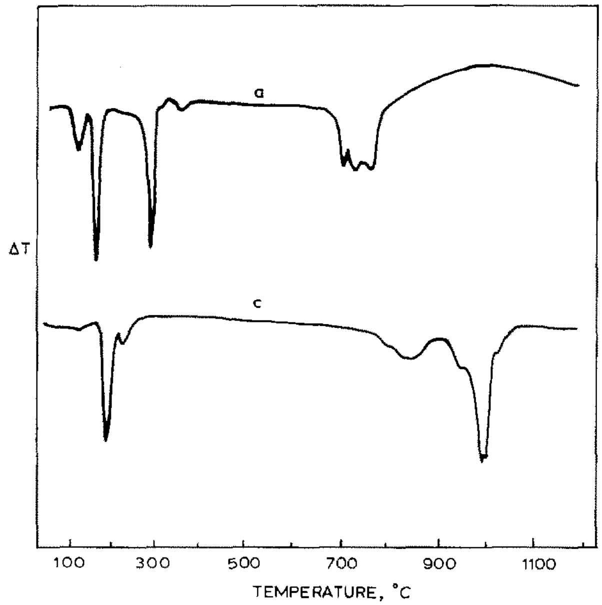

Fig. 2. DTA curves of magnesium and calcium selenate hydrates, diluted to 20% with α-alumina (heating rate 12.5 °C min^{-1}).

inside a furnace near a thermocouple of chromel–alumel with a 0 °C junction, connected to a Weston 3.5-digits digital voltmeter. After heating, the content in selenite ion in these samples was determined iodometrically [8]. The content of selenite ion in the samples heated up to 550, 740 and 850 °C was 6.7, 45.5 and 95.6% respectively, showing the formation at 750 °C of an intermediate compound nearly represented by the formula $CaSeO_4 \cdot CaSeO_3$.

Finally, the calcium selenite undergoes thermal decomposition to calcium oxide in a single step between 940 and 1150°

The DTA curve of the calcium selenate hemipentahydrate [Fig. 2c] shows only endothermic peaks. The first small peak at 110 °C, probably due to a crystalline transition, is followed by a peak at 180 °C which corresponds to the first mass loss of the TG curve. The third small peak at 220 °C is probably due to structural rearrangements ocurring after partial dehydration. There is no peak corresponding to the loss of 0.5 H_2O observed in the TG curve [Fig. 1c] between 250 and 350 °C.

The peak at 840 °C corresponds to the mass losses observed between 680 and 820 °C in the TG curve caused by the reduction of selenate to selenite ion. The shoulder at 800 °C of that peak is probably additional evidence of the formation of the intermediate compound shown by the TG curve.

The last peak at 1000 °C is due to the thermodecomposition of calcium selenite to calcium oxide, and corresponds to the last mass loss observed in the TG curve.

The TG and DTA curves of the calcium selenate hemipentahydrate [Figs. 1c and 2c] permit it to be suggested that the successive reactions of the thermal decomposition can be represented by the following sequence of steps

$$\begin{tikzcd}
2CaSeO_4 \cdot 2.5H_2O \arrow[r] & 2CaSeO_4 \cdot 0.5H_2O \arrow[r] & 2CaSeO_4 \arrow[d] \\
2CaO & 2CaSeO_3 \arrow[l] & CaSeO_4 \cdot CaSeO_3 \arrow[l]
\end{tikzcd}$$

CONCLUSIONS

The TG and DTA curves revealed a great difference in the thermal behaviours of the magnesium and calcium selenate hydrates. It was possible to establish the formation, in the case of calcium selenate, of an intermediate compound not yet described.

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