

Note

Thermal decomposition of magnesium selenate hexahydrate

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The isothermal dehydration of magnesium selenate hexahydrate was reported by Selivanova et al.¹ and Klein². There has, however, not been any investigation on thermogravimetry (TG), differential thermal analysis (DTA), and differential thermogravimetry (DTG) of magnesium selenate hydrate. This communication, which forms a part of a study dealing with thermal decomposition of metal selenate hydrates^{3,4}, presents the results of the complete thermal analysis of the title compound.

EXPERIMENTAL

Magnesium selenate hexahydrate, $\text{MgSeO}_4 \cdot 6\text{H}_2\text{O}$ was prepared by neutralising laboratory grade selenic acid with an excess of AnalaR grade magnesium carbonate, subsequent concentration of filtered solution, followed by crystallisation over P_2O_5 . The crystallised salt was chemically analysed on metal and selenate contents. The decomposition of magnesium selenate hexahydrate was investigated by thermoanalytical techniques as described previously⁴.

RESULTS AND DISCUSSION

Figure 1 shows results of typical thermograms of magnesium selenate hexahydrate. It is seen from the TG curve that the salt begins to lose water steadily and the process continues up to 115°C. At this stage a loss corresponding to one molecule of water occurs. This endothermic effect gives a DTA peak at 105°C. The pentahydrate formed does not appear to be much stable, since it immediately starts losing weight. At 170°C a loss corresponding to two molecules of water occurs and is associated with an endothermic peak at 130°C in the DTA curve. Magnesium selenate trihydrate which is comparatively more stable, starts losing weight and the remaining water molecule starts coming off. The salt is almost converted to anhydride at 360°C and the endothermic peak at 255°C represents this dehydration. However, this is followed by a sharp symmetrical exothermic peak with a maximum at 335°C. This may probably be due to the crystallisation of the anhydride just after its formation.

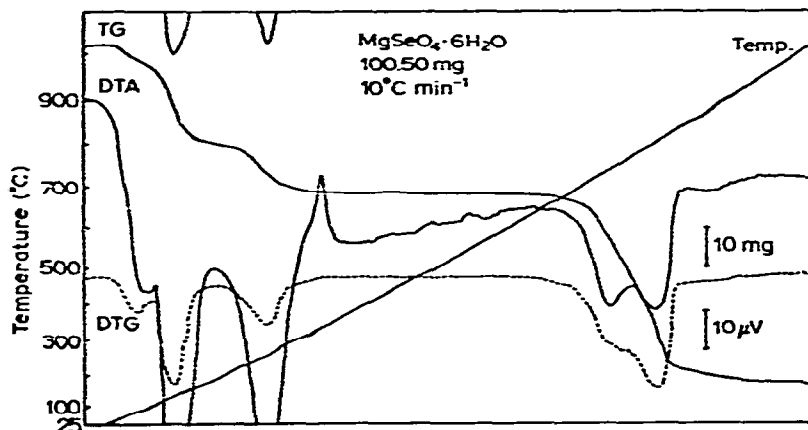
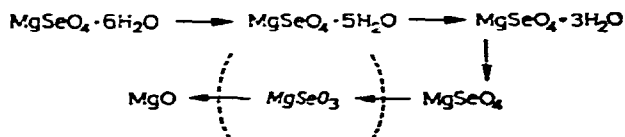


Fig. 1. Simultaneous TG-DTA-DTG of $\text{MgSeO}_4 \cdot 6\text{H}_2\text{O}$.

Magnesium selenate anhydride, which is quite stable over a long temperature range (as indicated by a horizontal plateau in TG curve running from 360 to 615°C), shows further decomposition beyond 615°C. The anhydride undergoes a reduction to selenite. The peak in the DTA curve associated with this process gives a maximum at 735°C. Subsequent decomposition of the selenite brings about the sublimation of selenium dioxide and quantitative formation of magnesium oxide. This endothermic effect is represented by a peak at 795°C. From the TG curve it appears that the decomposition of magnesium selenate anhydride to oxide is only a one-stage process. A critical study of the DTG curve in the region 735–800°C, however, makes it clear that two successive simultaneous losses occur as seen from partial overlapping of two peaks. Moreover, two distinct endothermic peaks as mentioned above account for this decomposition. Conversion to magnesium oxide is complete at 880°C.

The following mechanism can thus be proposed for the decomposition of magnesium selenate hexahydrate:



The agreement between the experimental weight changes obtained from the thermogravimetric results given in Table 1, and the weight changes predicted is excellent, thus supporting the proposed mechanism.

The above decomposition mechanism involves neither the formation of $2\text{MgSeO}_4 \cdot 9\text{H}_2\text{O}$ and dihydrate as observed by Klein² nor of tetrahydrate and monohydrate as proposed by Selivanova et al.¹, during the isothermal dehydration of magnesium selenate hexahydrate. On the contrary the trend of decomposition of the corresponding sulphate observed by Fruchart and Michel⁵ is in agreement with the

TABLE I
THERMOGRAVIMETRIC RESULTS OF $\text{MgSeO}_4 \cdot 6\text{H}_2\text{O}$

Dehydration/decomposition transition	Temp. ($^{\circ}\text{C}$)	Percentage loss	
		Theor.	Exp.
$\text{MgSeO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgSeO}_4 \cdot 5\text{H}_2\text{O}$	115	5.92	5.82
$\text{MgSeO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{MgSeO}_4 \cdot 3\text{H}_2\text{O}$	170	19.62	19.59
$\text{MgSeO}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{MgSeO}_4$	360	39.24	39.05
$\text{MgSeO}_4 \rightarrow \text{MgO}$	880	85.37	84.55

present investigation. Further, these authors have also observed the formation of pentahydrate and trihydrate of magnesium sulphate, analogous to the observation in the present work. They were not able to isolate magnesium oxide till 1100°C , the formation of which was complete at 880°C in the case of magnesium selenate hexahydrate. This is consistent with the general expectation that selenates are less stable than the corresponding sulphates.

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