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Note

THERMAL DECOMPOSITON OF ALKALI METAL SELENATES

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Some data related to the thermal decomposition of alkali metal selenates have already been reported. Gattow [1] studied the crystalline structure of K_2SeO_4, Rb_2SeO_4 and Cs_2SeO_4, reporting that $\beta \rightarrow \alpha$ transitions of these substances occur at 472, 552 and 587°C, respectively. Selivanova et al. studied the thermal decomposition of $Li_2SeO_4 \cdot H_2O$ [2], Rb_2SeO_4 [3], $CsSeO_4$ [4] and $Na_2SeO_4 \cdot 10\ H_2O$ [5] through their heating curves. The $Li_2SeO_4 \cdot H_2O$ heating curve presented endothermic effects at 156—190°C, due to the loss of H_2O and partial reduction of Se(VI) to Se(IV); at 680—690°C, due to fusion of Li_2SeO_4; and at 840°C, due to decomposition to $Li_2SeO_3 + 0.5\ O_2$. The heating curve of Rb_2SeO_4 showed an allotropic transformation at 540°C and fusion without decomposition at 1050°C. The heating curve of Cs_2SeO_4 exhibited two endothermic effects: at 608°C, ascribed to polymorphic transformation of rhombic to hexagonal form, reversible on cooling; and at 985°C, corresponding to fusion. In the case of $Na_2SeO_4 \cdot 10\ H_2O$, the formation of the anhydrous salt at 35°C was observed; the heating curve of Na_2SeO_4 showed a polymorphic transition at 600°C, fusion at 780°C and rapid decomposition above 1100°C, according to the equation

$$2\ Na_2SeO_4 \rightarrow Na_2O + Na_2SeO_3 + SeO_2 + O_2$$

The lack of TG and DTA data for alkali metal selenates suggested the present TG and DTA study of these compounds up to 1250°C.

EXPERIMENTAL

The alkali metal selenates were prepared by neutralization of hot water solutions of the corresponding alkali metal carbonates with a 25% water solution of freshly prepared selenic acid [6]. The final neutralization was

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carried out in a cold solution in the absence of CO_2. The resulting neutral solutions were dried in a water bath, and the crystals were kept in a desiccator containing anhydrous calcium chloride until constant weight was obtained.

The TG curves were obtained using a Deltatherm thermobalance D-4000-16, equipped with a Cahn Balance Model RH. A Pt/Pt—Rh 13% thermocouple was used as furnace temperature detector. Ca. 7 mg of material were placed in a 0.3 ml platinum crucible and heated at a rate of 5.2°C min^{-1} inside a ceramic hang-down tube in a static air atmosphere at ambient pressure.

The DTA curves were obtained in a Deltatherm D-2000-16 four-channel DTA module. Pt/Pt—Rh 13% differential thermocouples and block temperature thermocouples were used. α-Alumina was used as reference material. The samples were diluted to 20% or 50% with α-alumina and about 500 mg of these dilutions and reference material were tightly and homogeneously packed in the cylindrical holes of the inconel block of the specimen-holder assembly. The heating rate was 9.0°C min^{-1} under a static air atmosphere at ambient pressure.

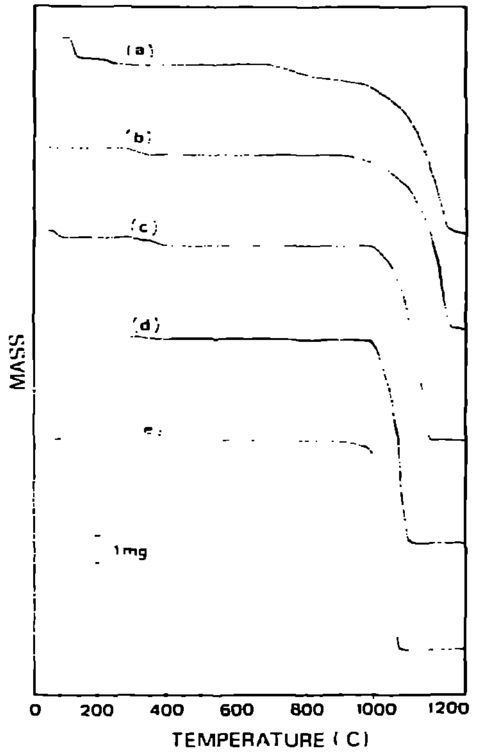
RESULTS AND DISCUSSION

Only rubidium and caesium selenates were obtained in anhydrous state. The thermal decomposition of the alkali metal selenates occurs in a characteristic way, as can be seen from the TG curves of Fig. 1 and the DTA curves of Fig. 2. All TG and DTA curves start at 25°C.

Between 120 and 250°C the TG curve of lithium selenate shows a loss of 13.1% water in two steps. This amount of water of crystallization corresponds to the formula $Li_2SeO_4 \cdot 1.30\ H_2O$. Between 650 and 850°C the fused lithium selenate suffers reduction to lithium selenite, as already reported, but this reduction does not seem to occur at lower temperatures [2]. Quantitative tests for the characterization of selenite in the presence of selenate failed to detect selenite in samples of lithium selenate previously heated at 400°C. The final mass loss beyond 900°C is probably due to partial evaporation and decomposition of the lithium selenite transformed to Li_2O and SeO_2. At 1180°C the residue of Li_2O corresponds to 14.1% of the anhydrous lithium selenate, meaning that about 74% of the lithium selenite formed decomposed to Li_2O and SeO_2.

Between 290 and 390°C the TG curve of sodium selenate shows a small mass loss of water (3.0%). This amount of water corresponds to the formula $Na_2SeO_4 \cdot 0.32\ H_2O$. The partial reduction of the fused sodium selenate to sodium selenite starts at 850°C. This reduction is not so evident through the TG curve as in the case of lithium selenate, probably because sodium selenite, being formed at a higher temperature, undergoes simultaneous evaporation and decomposition to Na_2O and SeO_2. At 1220°C the residue corresponds to 10.0% of the sodium selenate, indicating that only about 32% decomposed.

The TG curve of potassium selenate shows a water loss of 2.6% between



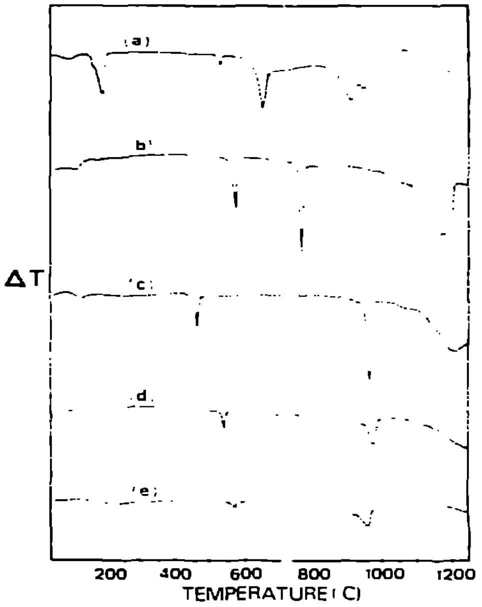


Fig. 1. TG curves of the alkali metal selenates obtained with a platinum crucible without cover. Heating rate: 5.2°C min^{-1}. (a) $Li_2SeO_4 \cdot 1.30\ H_2O$ (7.68 mg); (b) $Na_2SeO_4 \cdot 0.32\ H_2O$ (7.04 mg); (c) $K_2SeO_4 \cdot 0.32\ H_2O$ (7.72 mg); (d) Rb_2SeO_4 (7.56 mg); and (e) Cs_2SeO_4 (7.50 mg).

Fig. 2. DTA curves of the alkali metal selenates diluted to 20% in α-alumina. Heating rate: 9.0°C min^{-1}. (a) $Li_2SeO_4 \cdot 1.30\ H_2O$; (b) $Na_2SeO_4 \cdot 0.32\ H_2O$; (c) $K_2SeO_4 \cdot 0.32\ H_2O$; (d) Rb_2SeO_4; and (e) Cs_2SeO_4.

35 and 65°C. This amount of water of crystallization corresponds to the formula $K_2SeO_4 \cdot 0.32\ H_2O$. The small mass loss observed between 300 and 400°C is the result of mechanical losses caused by intense crepitation of the small crystalline particles of anhydrous potassium selenate. This mass loss did not appear in TG curves obtained with samples of potassium selenate previously ground and diluted to 50% with α-alumina and using a covered platinum crucible. The rapid mass loss at 990°C immediatley after fusion is probably due to evaporation. The residue at 1170°C is practically zero.

Between 330 and 340°C the TG curve of anhydrous rubidium selenate shows a small mass loss which is due to mechanical losses caused by crepitation of the crystals. As in the case of potassium selenate, this mass loss did not appear in TG curves obtained with samples of rubidium selenate previously ground and diluted to 50% in α-alumina and using a covered platinum crucible. At 950°C a rapid mass loss starts immediately after fusion, caused by evaporation of the melted salt. At 1110°C the residue is almost zero.

The TG curve of anhydrous caesium selenate shows that this compound has great thermal stability up to 900°C. At higher temperatures it undergoes

TABLE 1

Temperatures of DTA peaks (all endothermic) of alkali metal selenates and their interpretation

Compound	Temp. of DTA peaks (°C)	Interpretation
$Li_2SeO_4 \cdot 1.30\ H_2O$	55	Crystalline phase transition
	184	Dehydration
	533	Crystalline phase transition
	656	Fusion
	909—946	Reduction to selenite and decomposition
$Na_2SeO_4 \cdot 0.32\ H_2O$	85—165	Crystalline phase transition
	(370) [a]	(Dehydration) [a]
	583	Crystalline phase transition
	774	Fusion
	1173	Decomposition and evaporation
$K_2SeO_4 \cdot 0.32\ H_2O$	109	Dehydration
	470	Crystalline phase transition
	971	Fusion
	1200	Evaporation
Rb_2SeO_4	539	Crystalline phase transition
	972	Fusion
Cs_2SeO_4	573	Crystalline phase transition
	954	Fusion

[a] Only detectable in samples of sodium selenate diluted to 50% in α-alumina.

rapid evaporation after fusion and at 1070° C no residue remains.

The DTA curves of all alkali metal selenates (Fig. 2) show only endothermic peaks; their temperatures and interpretation are summarized in Table 1. These data are in accordance, within small temperature variations, with the data reported in the literature [1—5], except the peaks at 156—190° C [2], which are probably due only to water loss and not water loss and reduction of Se(VI) to Se(IV). The following peaks have not yet been described: the small peaks of lithium selenate at 55 and 540° C, probably due to crystalline phase transitions of the hydrated and anhydrous salt, respectively; the two small peaks of sodium selenate at 85 and 165° C, probably due to crystalline phase transitions; the great peak at 1173° C, corresponding to its final and simultaneous decomposition and evaporation; the three peaks of potassium selenate at 109° C, probably due to dehydration, at 970° C, due to fusion, and at 1200° C, due to its partial decomposition and evaporation.

The DTA curve of sodium selenate diluted to 20% in α-alumina does not show any peak between 300 and 400° C but the DTA curve obtained using sodium selenate diluted to 50% in α-alumina showed a small endothermic peak at 370° C (not yet described).

DTA curves of rubidium and caesium selenates diluted to 50% in α-alumina did not show any peak between 300 and 400° C.

REFERENCES

1 G. Gattow, Acta Crystallogr., 15 (1962) 419; Chem. Abstr., 56 (1962) 10614.
2 N.M. Selivanova and T.A. Sasykina, Zh. Neorg. Khim., 7 (1962) 240; Chem. Abstr., 56 (1962) 13784.
3 N.M. Selivanova, G.A. Zubova, A.A. Kalinkina and T.A. Sasykina, Izv. Vyssh. Mchebn. Zaved., Khim. Khim. Tekhnol., 5 (1962) 524; Chem. Abstr., 58 (1963) 7384.
4 N.M. Selivanova, T.A. Sasykina and G.A. Zubova, Izv. Vyssh. Mchebn. Zaved., Khim. Khim. Tekhnol., 5 (1962) 859; Chem. Abstr., 58 (1963) 11968.
5 N.M. Selivanova, T.A. Sasykina and I.S. Strel'tzov, Izv. Vyssh. Mchebn. Zaved., Khim. Khim. Tekhnol., 7 (1964) 365; Chem. Abstr., 61 (1964) 14170.
6 L.L Gilbertson and G.B. King, in L.F. Audrieth (Ed.), Inorganic Syntheses, Vol. III, McGraw-Hill, New York, 1950, p. 130.