

**KINETICS OF DEHYDRATION AND THERMAL
DECOMPOSITION OF $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
AND ITS DEUTERATED ANALOGUE WITH A VIEW
TO OBTAINING SrO**

M. Maneva and N. Petroff

HIGHER INSTITUTE OF CHEMICAL TECHNOLOGY, 1156 SOFIA, BULGARIA

The kinetics and mechanism of thermal dehydration of $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and its deuterated analogue were studied by means of DTA, TG and DSC. The temperatures, enthalpies and weight losses of phase transitions were measured. The dehydration occurs in a stepwise manner, and the composition of the intermediate depends on the rate of thermal decomposition. The kinetic parameters (E^* and Z) for the two steps of dehydration at a heating rate of 5 deg min^{-1} were calculated. A correlation was found between the dispersity of the end-product of the thermal decomposition (SrO) and the conditions of its preparation.

The mechanism of thermal decomposition of $\text{Sr}(\text{NO}_3)_2$ has been studied previously. However, there are no data on the dehydration and thermal decomposition of $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and it was thus of interest to study the kinetics of thermal dehydration and the enthalpies of the phase transitions of this compound, identified by DTA and DSC methods. The data were complemented with those obtained for the deuterated hydrate of $\text{Sr}(\text{NO}_3)_2$. A correlation was found between the dispersity of the SrO obtained as the end-product of the thermal decomposition the conditions of the process.

Experimental

The $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (I) and $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$ (II) used in the investigation were prepared by double recrystallization of p.a. grade $\text{Sr}(\text{NO}_3)_2$ from solutions in ordinary water or in heavy water at a temperature below 15° . The compounds were kept in an inert atmosphere. They were identified by measuring the strontium [6] and water contents.

The TG and DTA curves of the compounds were recorded with a Netzsch 429

apparatus at three different heating rates: 2.5 and 10 deg min⁻¹ in open ceramic crucibles and under an ambient atmosphere. The sample weight was 100 ± 1 mg.

The DSC curves were recorded with a Mettler apparatus at a heating rate of 5 deg min⁻¹ in open aluminium crucibles.

Results and discussion

The DTA data (Fig. 1) show that I dehydrates in a stepwise manner in the temperature range from 32° up to 185°. The deuterated analogue (Fig. 2) behaves in a similar way, the process ending at 195°. The two endoeffects observed with

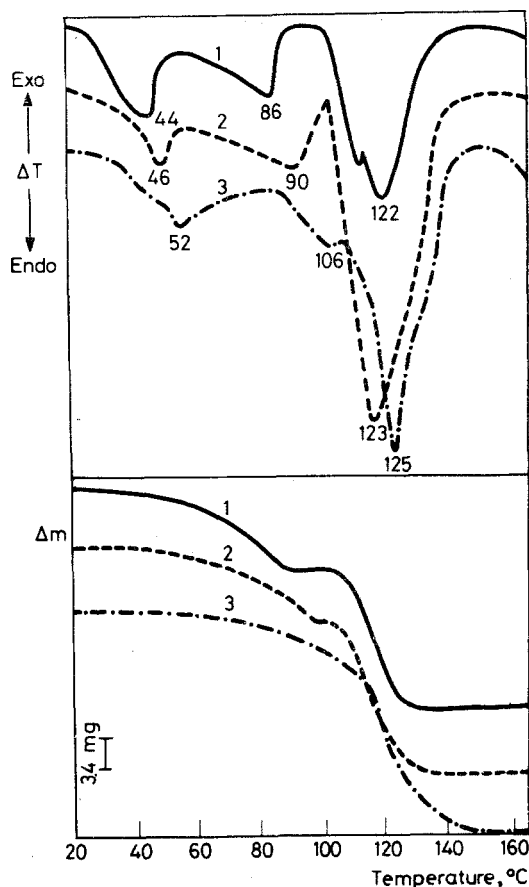


Fig. 1 DTA and TG curves of $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at heating rate: curve 1–2 deg/min.; curve 2–5 deg/min.; curve 3–10 deg/min. sample size 100 mg

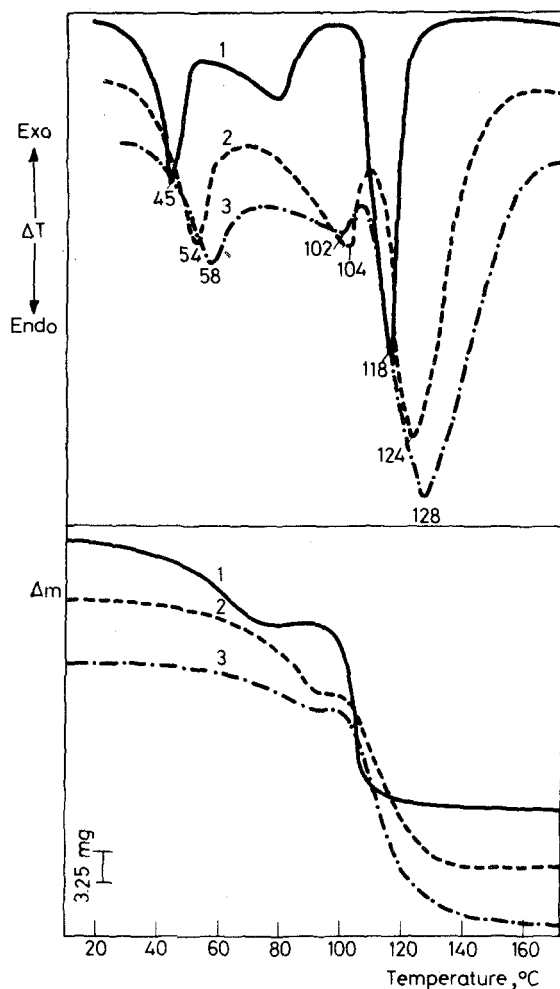


Fig. 2 DTA and TG curves of $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$ at heating rate: curve 1–2 deg/min.; curve 2–5 deg/min.; curve 3–10 deg/min. Sample size 100 mg

maxima at 44° and 86° for I at a heating rate of 2 deg min^{-1} correspond to the first step of dehydration. The low temperature of the beginning of this process allows the dehydration and evaporation of the hydrate water to be recorded separately, i.e. the sample melts in its crystal water. This is confirmed visually on the thermal treatment of I. The recorded decrease of weight in the TG curves (Δm) is greater than the theoretical one for the removal of one molecule of hydrate water. The deviation from the theoretical value is due to the further decomposition of the intermediate hydrate into a lower one or into an anhydrous salt. Correspondingly

the second step of dehydration, recorded as the third endoeffect, at 122° (Fig. 1, Table 1), gives a mass loss Δm of from 15.4% to 18.5%, i.e. smaller than the theoretical one for the removal of three molecules of hydrate water ($\Delta m = 19\%$). The overall mass loss measured by TG equals the theoretical content of water in I ($\Delta m = 25.4\%$). At the lowest heating rate (2 deg min⁻¹), a delay is observed in the temperature range from 88° up to 106°. In this range an intermediate appears to be stable, but its content of hydrate water depends strongly on the conditions of the experiment; for the heating rates investigated it varies from 2.5 upto 2.9 mol/mol Sr(NO₃)₂. During attempts to analyse the intermediate by the methods of IR spectral and X-ray diffraction analysis, it underwent changes, and accordingly it could not be established whether the intermediate is a hydrate with a nonintegral number of water molecules or a mixture of hydrates. The data given in Fig. 2 and Table 1 show that the first step of dehydration for II at a heating rate of 2 deg min⁻¹ occurs analogously to that for I, and the intermediate is stable in the temperature range from 85° up to 105° (TG curves). At the different heating rates, the content of hydrate water for II varies from 2.6 up to 3.0 mol/mol Sr(NO₃)₂.

Table 1 TG and DTA data on Sr(NO₃)₂·4H₂O (I) and Sr(NO₃)₂·4D₂O (II)

Sample	Phase transition	Δm theor., %	Heating rate, deg min ⁻¹	$T_{\text{init.}}-T_{\text{fin.}}$, °C (DTA)	T_{max} , °C	Δm , %	H ₂ O D ₂ O mol
I	Sr(NO ₃) ₂ ·4H ₂ O → →Sr(NO ₃) ₂ ·nH ₂ O + (4-n) H ₂ O	6.4	2	32-98	44 86	10	1.5
			5	32-105	46 90	8.8	1.4
			10	32-108	52 105	6.9	1.1
	Sr(NO ₃) ₂ ·nH ₂ O → →Sr(NO ₃) ₂ +n H ₂ O	19	2	105-155	122	15.4	2.5
			5	105-165	123	16.6	2.6
			10	108-185	125	18.5	2.9
II	Sr(NO ₃) ₂ ·4D ₂ O → →Sr(NO ₃) ₂ ·nD ₂ O + (4-n) D ₂ O	6.9	2	32-100	45 82	8.0	1.2
			5	32-108	54 102	9.8	1.4
			10	32-110	58 104	7.0	1.0
	Sr(NO ₃) ₂ ·nD ₂ O → →Sr(NO ₃) ₂ +n D ₂ O	20.6	2	105-142	118	19.5	2.9
			5	108-175	124	17.7	2.6
			10	110-195	128	20.5	3.0

The observed endoeffect with maximum at 122° (curve 1, Fig. 1) corresponds to the second step of dehydration, to anhydrous $\text{Sr}(\text{NO}_3)_2$. At the lowest heating rate (2 deg min^{-1}), the peak characterizing this effect is split, and a slight bend in the TG curve corresponds to it. This can be explained by stepwise removal of the remaining water molecules, which is not registered neither at higher heating rates nor for the deuterated product. From the TG data (Figs 1 and 2) we determined the kinetic parameters (E^* and Z) of the thermal dehydrations of the compounds by means of an algorithm, discusses in [7]. The main equation of nonisothermal kinetics is used in a logarithmic form:

$$\ln \frac{d\alpha/dT}{f'(\alpha)} = \ln (Zb^{-1})' - E^*/RT$$

For the first step of dehydration, the equation is of a diffusion type:

$$f'(\alpha) = -\ln(1-\alpha)^{-1}$$

For the second step of dehydration, the equation is an accelerating-type

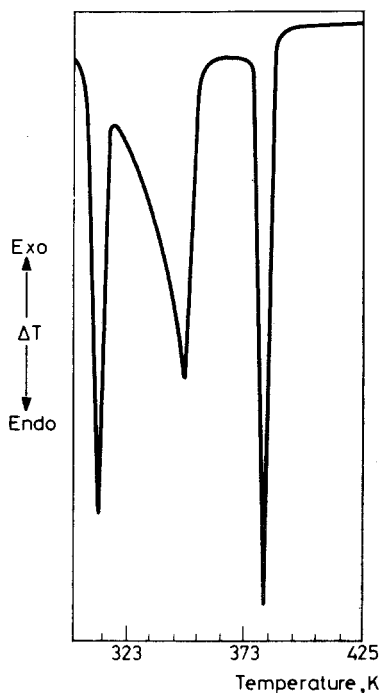


Fig. 3 DSC for $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at a heating rate of 5 deg/min

exponential law [8]:

$$f'(\alpha) = \alpha$$

At a heating rate of 5 deg min^{-1} , the following values were obtained for the kinetic parameters:

For the first step of dehydration:

$$E^* = 109 \pm 2 \text{ kJ/mol} \quad Z = 2.6 \cdot 10^{13} \text{ s}^{-1} \quad (\text{for I})$$

$$E^* = 115 \pm 2 \text{ kJ/mol} \quad Z = 8.3 \cdot 10^{13} \text{ s}^{-1} \quad (\text{for II})$$

For the second step of dehydration:

$$E^* = 172 \pm 2 \text{ kJ/mol} \quad Z = 2.8 \cdot 10^{22} \text{ s}^{-1} \quad (\text{for I})$$

$$E^* = 168 \pm 2 \text{ kJ/mol} \quad Z = 3.1 \cdot 10^{22} \text{ s}^{-1} \quad (\text{for II})$$

The DSC curves again show that the dehydration occurs stepwise (Figs 3 and 4, Table 2). Three endoeffects are observed, with peaks at 38° , 76° and 111° , respectively for I, and at 41° , 85° and 121° , respectively for II. The first two correspond to the first step of dehydration, and the third one to the second step of dehydration. The enthalpies recorded (ΔH°) are given in Table 2. It is noteworthy that the overall enthalpy of dehydration of II is greater than that of I 18.9 kJ mol^{-1} .

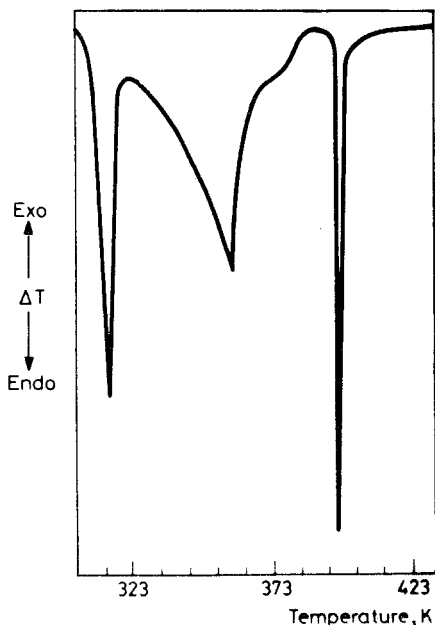


Fig. 4 DSC for $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$ at a heating rate of 5 deg/min

Table 2 DSC data on (I) and (II)

Sample	Step	Phase transition	$T_{\text{init.}}-T_{\text{fin.}}$, °C	T_{max} , °C	$\Delta H_{\text{ph.tr.}}^{\circ}$ (DSC)	$\Delta H_{\text{deh.}}^{\circ}$
I	1	$\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \rightarrow$ $\rightarrow \text{Sr}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O} +$ $(4-n) \text{H}_2\text{O}$	32-82	38 76	28.9 52.6	131.1
	2	$\text{Sr}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O} \rightarrow$ $\rightarrow \text{Sr}(\text{NO}_3)_2 + n \text{H}_2\text{O}$	103-116	111	49.6	
II	1	$\text{Sr}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O} \rightarrow$ $\rightarrow \text{Sr}(\text{NO}_3)_2 \cdot n\text{D}_2\text{O} +$ $(4-n) \text{D}_2\text{O}$	35-109	41 85	28.0 97.0	151.0
	2	$\text{Sr}(\text{NO}_3)_2 \cdot n\text{D}_2\text{O} \rightarrow$ $\rightarrow \text{Sr}(\text{NO}_3)_2 + n \text{D}_2\text{O}$	117-127	121	25.0	

The anhydrous salt remaining after the dehydration was stable up to 565°, but then decomposed to SrO. The products obtained at different heating rates from I and II were characterized by means of electron microscopy. At heating rates of 2 deg min⁻¹ and 10 deg min⁻¹, the average size of SrO particles obtained from II was about half that of those obtained from I, i.e. 0.3 µm from II and 0.6 µm from I at 2 deg min⁻¹ and 0.2 µm from II and 0.4 µm from I at 10 deg min⁻¹. A good degree of homogeneity was observed.

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Zusammenfassung — Kinetik und Mechanismus der thermischen Entwässerung von $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ und der deuterierten Verbindung $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$ wurden mittels TG-DTA und DSC untersucht. Temperaturen, Enthalpien und Gewichtsverluste der Phasenumwandlungen wurden gemessen. Der Prozess verläuft stufenweise, die Zusammensetzung des Zwischenprodukts hängt von der Zerset-

zungsgeschwindigkeit ab. Die kinetischen Parameter E^* und Z der beiden Entwässerungsstufen bei einer Aufheizgeschwindigkeit von 5 Grad min^{-1} wurden berechnet. Zwischen der Dispersität des Endproduktes SrO und seinen Bildungsbedingungen wurde eine Korrelation gefunden.

Резюме — Методом ТГ, ДТА и ДСК изучена кинетика и механизм термической дегидратации тетрагидрата нитрата стронция и его дейтерированного аналога. Измерены температуры и энтальпии фазовых переходов. Процесс дегидратации протекает ступенчато, а состав образующегося промежуточного продукта зависит от скорости термического разложения. Для двух стадий дегидратации, проведенных при скорости нагрева 5 К/мин , были вычислены кинетические параметры E и Z . Установлена корреляция между дисперсностью конечного продукта разложения оксидом стронция и условиями его получения.