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INVESTIGATION OF DEHYDRATION PROCESSES III. THERMAL DEHYDRATION OF STRONTIUM IODIDE HYDRATES

É. Buzágh-Gere, J. Sztatisz and S. Gál

Institute for General and Analytical Chemistry, Technical University Budapest, Hungary

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The dehydration phenomena of strontium iodide with different crystal water contents, prepared at room temperature, were studied with thermogravimetry and differential scanning calorimetry. The existence of strontium iodide dihydrate was proved during the dehydration of samples containing less then six moles of crystallization water. Evidence is given for the appearance of a liquid phase in the dehydration of strontium iodide dihydrate. The pertinent enthalpy values are reported.

Several hydrates of strontium iodide have been described in the literature. The forms containing 6, 2 and 1 molecules of combined water were identified using equilibrium methods [1]. Thermoanalytical studies in argon by Pekhkovsky and Sofronova [2] indicated the successive evolution in separate steps of 2, 2, 1 and 1 molecules of water in the course of heating, that is, it should be assumed that hydrates with 4, 2 and 1 molecules, resp., of combined water are present. In the thermogravimetric measurements carried out by Mirza and Karkhanavala [3] in air, only intermediates containing 4 and 1 molecules, resp., of combined water were observed, whereas Lutz and co-workers [4], using DTA and IR spectrometric techniques in argon, could only detect the existence of $SrI_2 \cdot 6\,H_2O$ and $SrI_2 \cdot H_2O$.

The starting material used by all cited authors was $SrI_2 \cdot 6\,H_2O$. The phenomenon well-known in the literature that the hydrate melts in its combined water was observed by Pekhkovsky and Sofronova at 82°, by Lutz and co-workers at 79° in the form of an endothermic effect. In one point all authors agree, namely that the combined water of strontium iodide monohydrate is evolved in a separate step, in the range between 280 and 370° depending on experimental conditions.

In our earlier studies [5] performed with $SrI_2 \cdot 6\,H_2O$ in its own gas atmosphere, the TG curve yielded a separate step only at the level corresponding to the monohydrate, while the DTA curve showed the peak of melting in the own combined water of the salt. On the DTA curve of the salt containing less than six moles of combined water, a further endothermic peak could be observed at a higher temperature than the former. This peak, according to preliminary studies carried out with DSC [5, 6] is in a reversely directed relationship with the combined water content. We therefore assumed that it is related to the percentage of a hydrate containing a lower number of water molecules combined. In the followings we shall report our results found in further studies of this pehnomenon.

Experimental

Material and method

The material used was Merck analytical grade and BDH analytical grade $SrI_2 \cdot 6\,H_2O$. The starting material was kept at ambient temperature in a desiccator containing P_2O_5 to yield strontium iodide preparations with various combined water contents.

The instruments used in measurements were a Du Pont Thermoanalyzer 990 with DSC cell and a Du Pont 951 thermogravimetric analyzer. The cell made of aluminium was internally coated with plastics to prevent an eventual interaction between strontium iodide and aluminium. Enthalpy changes were measured in airproof, sealed cells with samples of about 7 mg, by heating to about 120° at a heating rate of 5°/min. The enthalpy change was calculated from the curve of the second heating. We then controlled the weight of the closed crucible and subsequently opened the lid of the sample holder, placed it on the thermobalance and immediately started recording of the thermogravimetric curve in argon (flow rate 10 l/h) at a heating rate of 2°/min. The combined water content of the sample was calculated from the result of this measurement.

Results and discussion

A characteristic series each of the DSC and TG curves obtained with hydrates containing different amounts of combined water are presented in Figs 1 and 2. Next to the DSC curves we indicated the total water content relative to SrI_2, calculated from the TG curve.

As soon as the combined water content exceeds the percentage corresponding to $2\,H_2O$, the peak around 73 . . . 80° characterizing the dissolution of $SrI_2 \cdot 6\,H_2O$ appears, indicating that the water content in excess to 2 mol combined water is present in the hexahydrate form. On the other hand, the peak at 107° disappears at the water percentage corresponding to 5 mole combined water. Hence the dehydration processes taking place at different water contents may be represented by the following scheme:

If $x \geq 6$:

(i) $SrI_2 \cdot x\,H_2O \rightarrow SrI_{2\,(solution)} + x\,H_2O_{(l)}$.

If $5 > x > 2$:

(iia) $SrI_2 \cdot x\,H_2O \rightarrow bSrI_{2\,(solution)} + (x-2)H_2O_{(l)} + (1-b)SrI_2 \cdot 2\,H_2O_{(s)}$;

(iib) $SrI_2 \cdot 2\,H_2O_{(s)} \rightarrow SrI_2 \cdot H_2O_{(s)} + H_2O_{(l)}$.

The numerical values are listed in Table 1. The total water content served as the basis to calculate the $SrI_2 \cdot 6\,H_2O$ and $SrI_2 \cdot 2\,H_2O$ content of the samples (col-

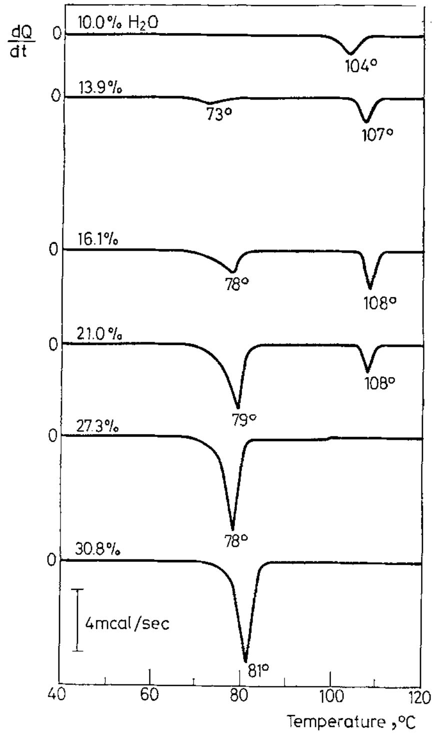

Fig. 1. DSC curves for strontium iodide hydrates with different amounts of combined water

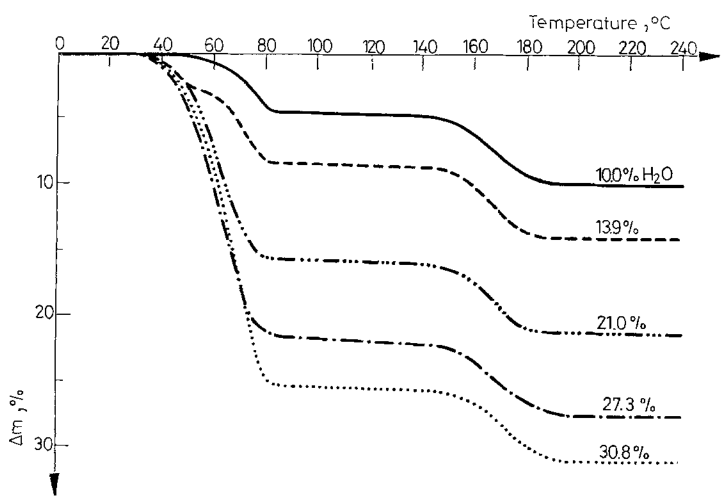

Fig. 2. TG curves for strontium iodide hydrates with different amounts of combined water

Table 1

Enthalpy change values for strontium iodide hydrates with different percentages of combined water

No. of sample	Water content, % (relative to SrI_2)	$SrI_2 \cdot 6\,H_2O$ content, %	$SrI_2 \cdot 2\,H_2O$ content, %	ΔH_{6H_2O}, J per (y per g) $SrI_2 \cdot 6\,H_2O$	ΔH_{2H_2O}, J per (y per g) $SrI_2 \cdot \cdot 2\,H_2O$
1	10.0	—	90.1	—	35.9
2	12.4	10.4	89.6	55.2	40.2
3	13.9	18.3	81.7	43.5	43.5
4	16.1	29.9	70.1	99.6	36.8
5	21.0	53.9	46.1	118.8	22.6
6	27.3	82.1	17.9	120.9	—
2	30.8	96.7	3.3	114.6	—
8	31.2	97.4	2.6	113.8	—

umns 3 and 4). The values of the enthalpy changes are listed in columns 5 and 6 relative to the mass units of these hydrates. With decreasing $SrI_2 \cdot 2\,H_2\,O$ content, the enthalpy change per mass unit of this hydrate shows a decreasing trend, and no enthalpy change was observed at 17.9% $SrI_2 \cdot 2\,H_2O$ content. To explain this finding, we started from the assumption that after $SrI_2 \cdot 6\,H_2O$ has melted in the combined water, at further increase of temperature a part of $SrI_2 \cdot 2\,H_2O$ will also be dissolved. On the basis of the solubility of SrI_2 we calculated the still remaining mass of $SrI_2 \cdot 2\,H_2O$ and recalculated the enthalpy change relative to this value. (In the computation we also took into consideration that no observable enthalpy change occurs at 17.9% $SrI_2 \cdot 2\,H_2O$.) From the above assumption the following value was found:

$$\Delta H_{SrI_2 \cdot 2H_2O} = 28.7 \pm 3\ \text{J/mole}.$$

The enthalpy change per mass unit assigned to the melting of $SrI_2 \cdot 6\,H_2O$ is also not constant when the proportion of the hexahydrate increases. We have not yet been able to find an acceptable explanation for this phenomenon. It might eventually be caused by some secondary relationship between $SrI_2 \cdot 2\,H_2O$ and $SrI_2 \cdot \cdot 6\,H_2O$. Therefore we determined the value of the enthalpy change taking place at the hexahydrate melting in its combined water from the DSC curves of the purest preparation at our disposal. The value obtained was

$$\Delta H_{SrI_2 \cdot 6H_2O} = 50.7 \pm 5\ \text{J/mole}.$$

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Résumé — On a étudié, par thermogravimétrie et analyse calorimétrique différentielle, la déshydratation de l'iodure de strontium contenant diverses sortes d'eaux de cristallisation préparé à température ambiante. On montre l'existence de l'iodure de strontium bihydraté formé lors de la déshydratation d'échantillons contenant moins de six molécules d'eau de cristallisation. On met en évidence l'apparition d'une phase liquide lors de la déshydratation de l'iodure de strontium bihydraté. Les enthalpies respectives sont données.

Zusammenfassung — Die Dehydratisierungserscheinungen von bei Zimmertemperatur hergestelltem Strontiumjodid mit verschiedenem Kristallwasser wurden durch Thermogravimetrie und Differential-Abtastkalorimetrie untersucht. Die Existenz von Strontiumjodid-Dihydrat wurde während der Dehydratisierung von weniger als 6 Mol Kristallwasser enthaltenden Proben bewiesen. Beweis für das Auftreten einer Flüssigphase während der Dehydratisierung von Strontiumjodid-Dihydrat wird erbracht. Die bezüglichen Enthalpiewerte werden angegeben.

Резюме — Явление дегидратации иодида стронция с различным содержанием кристаллизационной воды было изучено с помощью термогравиметрии и дифференциальной сканирующей калориметрии. При дегидратации образцов, содержащих меньше чем шесть молекул кристаллизационной воды, доказано существование дигидрата иодида стронция. Представлено доказательство появления жидкой фазы при дегидратации дигидрата иодида стронция. Сообщены подходящие значения энтальпии.