Journal of Thermal Analysis, Vol. 4 (1972) 293—298

INVESTIGATION OF THE THERMAL DECOMPOSITION OF SOME PERIODATES BY MEANS OF EMANATION THERMAL ANALYSIS (ETA) AND DTA

V. BALEK and J. JULÁK*

Department of Radiochemistry, Charles University, Prague;
**Department of Inorganic Chemistry, Charles University, Prague, Czechoslovakia*

(Received September 20, 1971)

Thermal decomposition of $Be_3(IO_5)_2 \cdot 12H_2O$, $Mg_2I_2O_9 \cdot 11H_2O$, $Ca_2I_2O_9 \cdot 9H_2O$ and $Ba_2I_2O_9 \cdot 9H_2O$ in the temperature interval of 20 to 600° was studied by means of emanation thermal analysis (ETA) and differential thermal analysis (DTA). The magnetic properties of decomposition intermediates of periodates studied are discussed.

Paramagnetic intermediates described recently as compounds of hexavalent iodine were found to be formed by thermal decomposition of some periodates [1]. It was proved [2] that the paramagnetism of the decomposition products is caused by the presence of molecular oxygen in the case of the periodates $Be_3(IO_5)_2 \cdot 12H_2O$, $Mg_2I_2O_9 \cdot 11H_2O$, $Ca_2I_2O_9 \cdot 9H_2O$ and $Ba_2I_2O_9 \cdot 9H_2O$. It was explained at the same time that these decomposition products consist of mixtures of I (V) and I (VII) compounds in different ratios. It may be assumed on the basis of study [2] that a relationship exists between the paramagnetism of the decomposition intermediates of the above-mentioned periodates and the degree of disorder of their structures. Since the paramagnetic decomposition products are mostly amorphous roentgenographically, the emanation method was chosen to study their degrees of disorder [3]. By this method the parent radioactive isotope is incorporated into the sample and the radioactive gas released from the solid substance by heating is carried by a carrier gas stream at a constant flow rate into cells for gas radioactivity measurement. Temperature rise, ETA and DTA curves are recorded. When no chemical or physical conversions take place within the solid, its rate of release of emanation is dependent on temperature only. The appearance of characteristic maxima on the release curve offers certain possibilities for the identification of the crystalline form and nature of the substance and provides indirect information on the structural arrangement (or disarrangement) of solids [4, 5].

The purpose of this work is to study the thermal decomposition of the above-mentioned periodates by means of emanation thermal analysis (ETA) and differential thermal analysis (DTA) under dynamic conditions in air. Decomposition intermediates in individual temperature ranges were characterized by means of magnetic susceptibility measurements, X-ray analysis and chemical analysis. These results were reported earlier [2].

* Present address: Institute for Medical Microbiology, Charles University, Prague.

Experimental

The preparation of the periodates the thermal decomposition of which was investigated, was described in a previous paper [2]. Samples were labelled with the parent isotope of emanation in an alcoholic ^{228}Th solution and dried in air. The resulting activity of the labelled samples was 0.01 μCi/g.

The ETA – DTA apparatus employed has been described previously [3]. The weight of samples taken was about 0.2 g, and the ETA results were converted to 1 g sample values. The heating rate was 5° per minute. The thermal decomposition of the samples was studied between 20 and 600° using air as the carrier gas.

Results

Beryllium periodate $Be_3(IO_5)_2 \cdot 12H_2O$ (Fig. 1). The effects on the ETA curve at 60° and on the DTA curve at 85° correspond to partial dehydration of the salt and formation of the octahydrate $Be_3(IO_5)_2 \cdot 8H_2O$. The thermal decomposition of this intermediate yields an endothermic peak on the DTA curve in the range 120 – 180° and a corresponding slight effect on the ETA curve. The effects on the ETA curve indicate the starting of these decomposition processes, since with the method of sample labelling employed, the emanation method provides information on the initial stages of topochemical processes in solids. Besides residual water, oxygen is liberated in this thermal decomposition process; this probably remains absorbed on the surface of the roentgenographically amorphous inter-

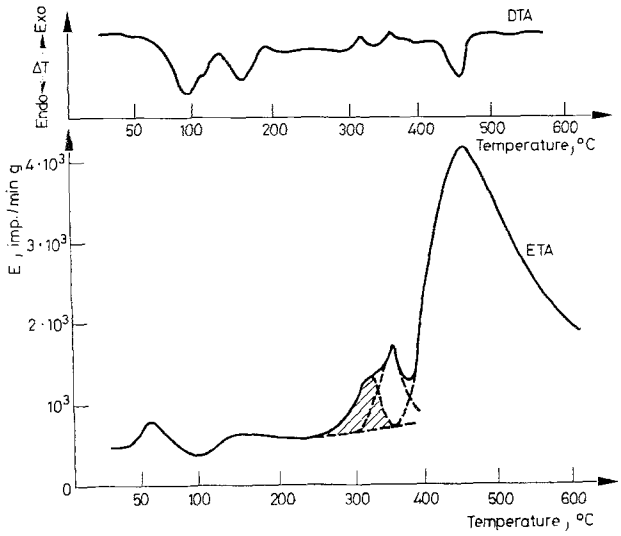

Fig. 1. ETA and DTA curves of $Be_3(IO_5)_2 \cdot 12H_2O$. The hatched peak on the ETA curve indicates the crystallization of $Be(IO_3)_2$

mediates and causes their paramagnetism. Crystalline products are gradually formed in the interval 300–375°, $Be(IO_3)_2$ being the first to crystallize from the amorphous $Be(IO_3)_2$ + 2BeO mixture (see the exothermic peak at 300°) while BeO crystallizes with some delay (exothermic peak at 350°). At the same time, the respective overlapping effects appear on the ETA curve and the paramagnetism of the decomposition intermediates disappears. Iodine is liberated and more crystalline BeO is formed at about 375°. This BeO is the final product of thermal decomposition of $Be_3(IO_5)_2 \cdot 12H_2O$ [2].

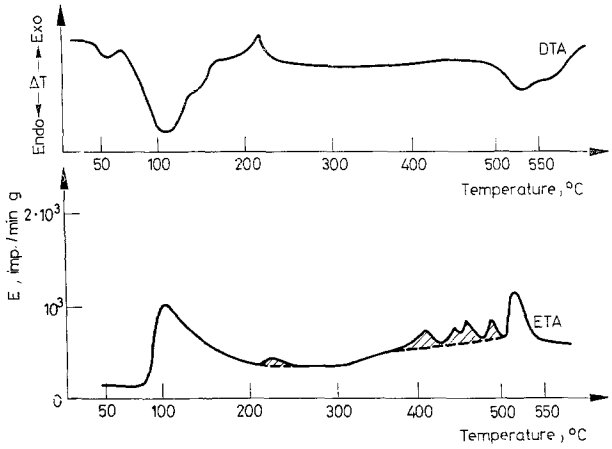

Fig. 2. ETA and DTA curves of $Mg_2I_2O_9 \cdot 11H_2O$. The hatched peaks on the ETA curve indicate the primary crystallization and later sintering of $Mg(IO_3)_2$

Magnesium periodate $Mg_2I_2O_9 \cdot 11H_2O$ (Fig. 2). The stepwise dehydration of the sample takes place up to about 110°, the nonahydrate and trihydrate being formed in turn. Both stages of dehydration are indicated on the DTA curve, whereas the ETA curve indicates the last stage only. The decomposition of the periodates starts at about 150° and continues up to 500°. In this temperature interval, oxygen and residual water are liberated, and primary crystallization of the gradually forming $Mg(IO_3)_2$ takes place: this product then sinters in the range 400–500°, as shown by the X-ray patterns. The exothermic peak on the DTA curve at 210° and the ETA effect at 210–230° indicate primary crystallization of $Mg(IO_3)_2$, while later sintering is only shown on the ETA curve in the range 380–500°. The X-ray patterns of the decomposition products before sintering are diffuse in character, whereas they exhibit sharp lines after sintering. Up to the beginning of the sintering process the decomposition products are weakly paramagnetic. The thermal decomposition of $Mg_2I_2O_9 \cdot 11H_2O$ is completed by the formation of MgO [6] with simultaneous liberation of iodine (see the endothermic DTA peak and the ETA peak at 500–550°).

Calcium periodate $Ca_2I_2O_9 \cdot 9H_2O$ (Fig. 3). Stepwise dehydration and decomposition of the periodate take place in the interval 100–150°. These processes are resolved on the ETA curve but cause a single endothermic effect on the DTA curve. With further heating of the sample, decomposition proceeds, with liberation of water and oxygen the oxidation stage of the iodine decreasing continuously. At 300–450°, $Ca(IO_3)_2$ crystallizes from these amorphous products (see the exo-

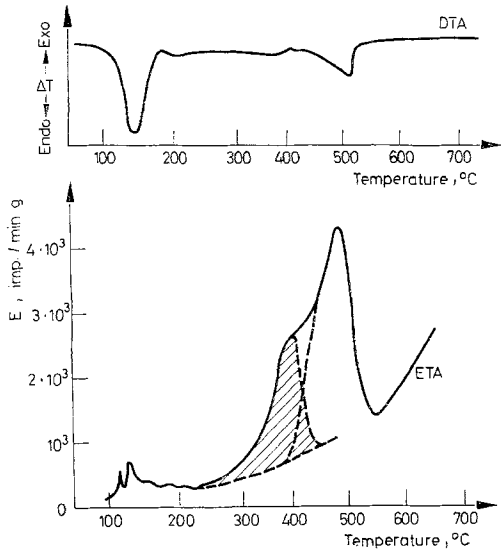

Fig. 3. ETA and DTA curves of $Ca_2I_2O_9 \cdot 9H_2O$. The hatched peak on the ETA curve indicates the crystallization of $Ca(IO_3)_2$

thermic effect on the DTA curve at 400° and the hatched effect on the ETA curve) The paramagnetism of the intermediates, caused by adsorbed oxygen, disappears simultaneously with the formation of this crystalline product. Decomposition of $Ca_2I_2O_9 \cdot 9H_2O$ is completed by formation of the orthoiodate $Ca_5(IO_6)_2$ – see the endothermic effect in the DTA curve and the ETA effect at 450–510°.

Barium periodate $Ba_2I_2O_9 \cdot 9H_2O$ (Fig. 4). Similarly to the preceding cases, partial dehydration starts above 100° with formation of the octahydrate: this is followed by periodate decomposition – see the ETA and DTA effects at 100–200°. The decomposition of the periodate results in amorphous products exhibiting paramagnetism, caused by oxygen adsorption. At 350–400° $Ba(IO_3)_2$ crystallizes from the amorphous intermediate mixture, as shown by the ETA and DTA effects and X-ray patterns. Crystallization is again accompanied by the disappearance of the paramagnetism of the decomposition products. The thermal decomposition of $Ba_2I_2O_9 \cdot 9H_2O$ is completed in the temperature range studied by the formation of $Ba_5(IO_6)_2$ [7].

As follows from the previous study [2] of the decomposition of periodates, the degree of crystallinity of their decomposition intermediates changes during the thermal treatment. The effects on the ETA curves, indicated by hatching in Figs 1–4, seem to be caused by these changes of crystallinity. As shown in [2], the intermediates of the thermal decomposition of the periodates studied are paramagnetic in certain temperature intervals. Their paramagnetism is due to the presence of O_2 in the sample. It also follows from this study that the temperature intervals of the appearance of the paramagnetic inter-

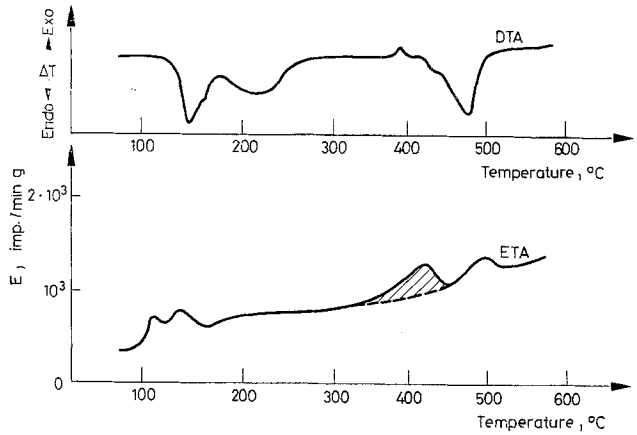

Fig. 4. ETA and DTA curves of $Ba_2I_2O_9 \cdot 9H_2O$. The hatched peak on the ETA curve indicates the crystallization of $Ba(IO_3)_2$

mediates correspond to the temperatures where roentgenographically amorphous intermediates were found. From a study of the magnetic properties of the above-mentioned intermediates [2] the Curie–Weiss law was found to be valid. The values of the Weiss constant measured at the temperature of liquid nitrogen were found for the roentgenographically amorphous intermediates of the decomposition of Be, Mg, Ca and Ba periodates as −25, −40, −21 and −32 °K (±2 °K), respectively. These magnetic properties are in good agreement with those in [5] where the association of oxygen, $2O_2 \leftrightarrow O_4$, was concluded. This association of oxygen molecules seems to be lowered or totally suppressed by fixation of O_2 molecules on the surface or lattice of the sample.

The sequence of the Weiss constant values for the intermediates of the thermal decomposition of the periodates is: Mg < Ba < Be < Ca. It is of interest that the same sequence was found by comparing the ETA effects (hatched in Figs 1–4) caused by changes of crystallinity of the samples studied.

References

1. DRÁTOVSKÝ M. and PAČESOVÁ L., Usp. chimii, 37 (1968) 537.
2. JULÁK J., Coll. Czech. Chem. Comm., in print.
3. BALEK V., J. Mat. Sci., 4 (1969) 919.
4. BALEK V., Anal. Chem., 42 (1970) 16A.
5. BALEK V., Z. anorg. allg. Chem., 380 (1971) 82.
6. MULAY L. N. and KEYS L. K., J. Am. Chem. Soc., 86 (1964) 4489.
7. DRÁTOVSKÝ M. and KOŠLEROVÁ J., Coll. Czech. Chem. Comm., 31 (1966) 4375.
8. DRÁTOVSKÝ M., Z. anorg. allg. Chem., 334 (1964) 169.

RÉSUMÉ — On a suivi la décomposition thermique de $Be_3(IO_5)_2 \cdot 12H_2O$, $Mg_2I_2O_9 \cdot 11H_2O$, $Ca_2I_2O_9 \cdot 9H_2O$ et $Ba_2I_2O_9 \cdot 9H_2O$ entre 20 et 600° par ATD et analyse des gaz. On discute les propriétés magnétiques des produits intermédiaires issus des periodates étudiés.

ZUSAMMENFASSUNG — Die thermische Zersetzung von $Be_3(IO_5)_2 \cdot 12H_2O$, $Mg_2I_2O_9 \cdot 11H_2O$, $Ca_2I_2O_9 \cdot 9H_2O$ und $Ba_2I_2O_9 \cdot 9H_2O$ wurde zwischen 20—600° durch Emanations- und Differentialthermoanalyse untersucht. Die magnetischen Eigenschaften der intermediären Zerfallsprodukte der Perjodate wurden ebenfalls untersucht und besprochen.

Резюме — С помощью эманационного термического анализа и дифференциального термического анализа (ДТА) исследован термораспад $Be_3(IO_5)_2 \cdot 12H_2O$, $Mg_2I_2O_9 \cdot 11H_2O$, $Ca_2I_2O_9 \cdot 9H_2O$ и $Ba_2I_2O_9 \cdot 9H_2O$ в температуры 20—600°. Обсуждаются магнитные свойства промежуточных продуктов распада изученных перйодатов.