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SIMULTANEOUS TG, DTG AND DTA ANALYSES IN CONTROLLED INERT GAS FLOW FOR THE DETERMINATION OF DEAQUATION STEPS OF POLYHYDRATED SULFATES

SARA SARIG
Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem (Israel)
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ABSTRACT

The thermal deaquation reactions of $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 7H_2O$ were studied by simultaneous TG, DTG and DTA. In the $CuSO_4 \cdot 5H_2O$ thermogram three distinct steps corresponding to 2 moles, 2 moles, 1 mole of water were observed, and in the $NiSO_4 \cdot 7H_2O$ the sequence 1 mole, 3 moles, 2 moles, 1 mole was determined. The deaquation steps were correlated with the structure of water of crystallization. An exothermic DTA peak was observed during the evolution of the first mole of water in $NiSO_4 \cdot 7H_2O$.

INTRODUCTION

The sequence of thermal deaquation reactions of several polyhydrated metal sulfates, as reported by Ben-Dor and Margalith[1], consists of two definite steps: First, all but one mole of water are evolved at relatively low temperatures (beginning at 60°C); then, after a significant rise in temperature, the last mole is evolved. All the intermediate monohydrates show characteristic acidic properties.

Tanabe et al.[2] used X-rays, infrared, NMR and ESR techniques in their investigations of nickel sulfate monohydrate, because of the special interest in its catalytic activity, which is closely related to the acidic properties.

The detection of intermediate compounds during the evolution of "all but one" moles of water is not easy because in many cases these steps overlap. The selectivity is, of course, dependent on experimental conditions. Fruchart and Michel[3] detected intermediate compounds when $NiSO_4 \cdot 7H_2O$ was heated and ascribed their success to the slow heating rate of 0.6°C min^{-1}. It is, however, questionable whether the heating rate alone is the decisive factor for detecting the separation of deaquation steps. Ben-Dor and Margalith[1] detected four definite steps in the DTA analysis of the initially evolving four moles of water during thermal decomposition of $CuSO_4 \cdot 5H_2O$ at a relatively high heating rate of 6°C min^{-1}, using the dynamic gas technique.

The determination of the number of water molecules evolved at each one of the early deaquation steps of $NiSO_4 \cdot 7H_2O$ as carried out by Fruchart and Michel[3], namely, 1 mole, 2 moles, 3 moles and 1 mole, which was tentatively accepted by

Tanabe et al.[2], may be erroneous. The DTA and TG measurement of Fruchart and Michel were carried out separately and under quite different experimental conditions[3]. Consequently, the temperatures of the DTA peaks and those of the very slight inflections of the TG curve were not identical and had to be somewhat arbitrarily correlated.

The correlation between DTA and TG curves is not always straightforward: two or even more DTA peaks may correspond to a single mass loss step, as was recently found by Wendlandt and Simmons[4] in the case of $BaCl_2 \cdot H_2O$ deaquation.

Paulik et al.[5], in their extensive study of the effect of experimental conditions on the reproducibility and the selectivity of thermal analyses results, stressed the importance of sample packing and layer thickness. They used a specially constructed polyplate holder in which the sample can be spread very thinly and carried out simultaneous TG, DTA and DTG measurements. Paulik detected three distinctive deaquation steps of $CuSO_4 \cdot 5H_2O$, namely, 2 moles, 2 moles and 1 mole of water, emphasizing that these separate steps could be distinguished only when using the polyplate holder.

In this work the three distinctive deaquation steps of $CuSO_4 \cdot 5H_2O$ were detected, using a simple micro-crucible. The decomposition was carried out on Mettler Thermoanalyzer in controlled dry nitrogen flow.

The deaquation of $NiSO_4 \cdot 7H_2O$ is also presented and leads to a different scheme of deaquation steps than that proposed by Fruchart and Michel[3] and tentatively adopted by Tanabe et al.[2] and others.

The sequence of deaquation steps of $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 7H_2O$ is to be correlated with the crystallographic structure of the water of crystallization in these substances as elucidated by recent X-rays and neutron diffraction studies and beautifully presented by Evans[6].

EXPERIMENTAL

Simultaneous DTA, TG and DTG determinations were carried out on Mettler Thermoanalyzer, under controlled dry nitrogen flow of 5 l/hr.

The samples ranged from 16.07 to 23.82 mg, and the heating rate from 1.5 to 4 °C min^{-1}. The "expanded weight" sensitivity used for TG measurements was 1 mg per recorder span but for clarity only the tenfold condensed weight loss signal was depicted on the diagrams. The DTA sensitivity was 50–100 μV and the DTG range 1 mg min^{-1} to 5 mg min^{-1}.

RESULTS AND DISCUSSION

Three weight-loss steps of $CuSO_4 \cdot 5H_2O$ (Fig. 1) accompanied by three DTG curves and by three corresponding endothermic DTA peaks can be distinguished at 85, 107 and 231 °C. The sample weight was 23.82 mg; therefore the theoretical weight loss on the evolution of one molecule of water should be 1.71 mg. The experimental values are as follows: the first step, AB, is 3.33 mg, the second, BC, is 3.32 mg and the last, DE, is 1.68 mg. These values verify the [2 moles, 2 moles, 1 mole] sequence of deaquation.

The rate of heating was 2°C min^{-1}.

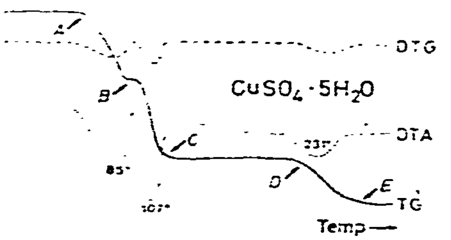

Fig. 1. Deaquation of cupric sulfate pentahydrate.

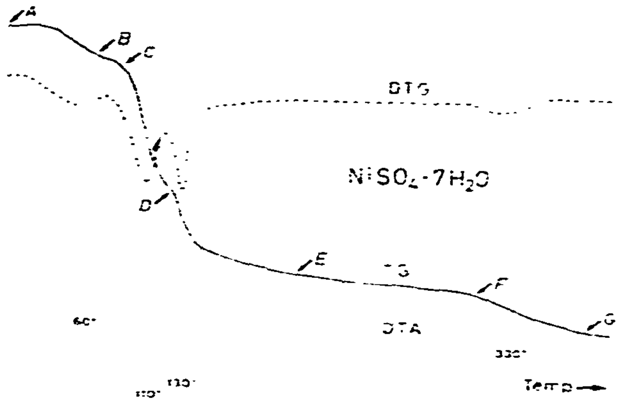

Fig. 2. Deaquation of nickel sulfate heptahydrate.

In Fig. 2 a representative sequence of deaquation steps in 21.30 mg $NiSO_4 \cdot 7H_2O$ sample at 2°C min^{-1} heating rate is shown. The demarcation between weight-loss steps is best distinguishable at heating rates lower than the 2°C min^{-1} employed, but then the DTA curve, especially at temperatures above 120°C, has a poor response. On the other hand, at heating rate of 4°C min^{-1}, the DTA peaks are narrow and well developed, but the weight-loss steps seem less sharply differentiated than those at low rates of heating. They can, nevertheless, be readily differentiated by their DTG curves. The regions like BC or EF on Fig. 2, in which there is gradual loss of water, which cannot properly be ascribed to a specific deaquation step. are the least pronounced the higher the rate of heating. In fact, the region BC does not appear at all on the 4°C min^{-1} heating rate thermogram.

The loss of one molecule of water in the 21.30 mg sample corresponds to the weight-loss of 1.37 mg. The respective weight losses of the steps in Fig. 2 are as follows: AB, 1.25 mg; CD, 4.35 mg; DE, 2.92 mg; FG, 1.35 mg. These results indicate the sequence of deaquation steps: 1 mole, 3 moles, 2 moles, and, finally, 1 mole.

The fit between the experimental weight-loss steps and the theoretically calculated ones of $NiSO_4 \cdot 7H_2O$ is not as good as in the case of $CuSO_4 \cdot 5H_2O$. The reason may be that $NiSO_4 \cdot 7H_2O$ crystals are actually poorly developed aggregates.

The first weight-loss step of $NiSO_4 \cdot 7H_2O$ is accompanied by an exothermic DTA peak, while the others are endothermic as would be expected. There are little data about the nature, or even the existence, of the DTA peak corresponding to the loss of the first water molecule. Thus, for instance, both Ben-Dor and Margalith[1] and Tanabe et al.[2] list $NiSO_4 \cdot 7H_2O$ as a starting material but report results concerning $NiSO_4 \cdot 6H_2O$ only.

An interesting correlation between the thermal and the crystallographic data can be found for the two investigated polyhydrated sulfates. It is known that in $CuSO_4 \cdot 5H_2O$, four molecules of water are coordinatively bonded to the cupric ion. But, although the water coordinated cupric ion is of a size comparable to that of the sulfate and both ions have the same charge, the structure of cupric sulfate is not a simple one: a fifth molecule of water is needed to fill certain "holes". The uncoordinated molecules form a network of their own, the so-called "structural water". The water molecules of both types form hydrogen bonds with the sulfate ions and among themselves. Because of the complexity of the structure, each water molecule has a different surrounding and, consequently, bonds of different length and strength. They may, however, be divided into three groups: (1) The water molecules, termed according to Evans[6], Aa and Ab, in addition to their coordinative bonds to Cu, form two hydrogen bonds with sulfate groups—altogether three bonds per molecule. (2) The molecules termed Ac and Ad, in addition to the three bonds already mentioned, form also a bond with the structural water—totaling four bonds per molecule. (3) The structural water molecule itself forms four bonds: two with the sulfate ions and two with the coordinated water molecules.

It seems therefore very plausible that the molecules of group (1), which have only three bonds to disrupt, are the first to come out. The molecules of group (2), tied up by four bonds, need more energy than those of group (1) to break them and therefore they evolve at higher temperature than those of group (1). After the four water molecules are gone, the last one presumably forms an SO_5H_2 group[1] and is therefore more persistent than the loosely bonded polyhydrate molecules.

The six coordinative water molecules of the nickel ion in $NiSO_4 \cdot 7H_2O$ have more varied surroundings than the four copper bonded molecules described. Four molecules in $NiSO_4 \cdot 7H_2O$ are situated almost in one plane. They are all termed "A" molecules, every one forming three bonds and can be divided into two sub-groups:

(a) Molecule Aa, bonded to Ni and to *one* sulfate ion by two bonds.

(b) Molecules Ac and Ad, bonded to Ni and to two sulfate ions, *i.e.*, bonded to three different species. Af also belongs to this group, thrice bonded: once to Ni and to two different water molecules.

The four bonded "B" class molecules can be also sub-divided:

(c) One of their four bonds is, of course, the coordinative oxygen–nickel bond. The molecule Bb is additionally bonded to two sulfate ions and to the structural water molecule, and Bc is bonded to one sulfate ion, to one coordinated water molecule from another cation's sphere and to the structural water.

(d) The structural water molecule Bg.

The thermogram of $NiSO_4 \cdot 7H_2O$ shows four distinct deaquation steps. The four different slopes of TG are augmented by four DTG peaks and have respective DTA peaks at the same temperatures: 60, 110, 130 and 330°C. These steps represent: (1) one molecule, which corresponds to the most weakly bonded molecule, Aa (2) three molecules, which seem to be Ac, Ad and Af, each of them having to break three bonds to three different species, (3) two molecules, Bb and Bc, with four bonds, and finally (4) the structural water molecule, Bg, which acquires the characteristic acidic properties of sulfate monohydrates.

It may be concluded that the thermogravimetric results presented here can be easily explained by the different number of bonds and their different strengths that the water molecules have to break, in order to escape from their respective hydrated sulfates.

The claim that the slower the rate of heating, the better the separation of deaquation steps[7] is, like any statement of this kind, restricted by the ever-present clause: "all other conditions being equal".

It seems that some of the "other conditions" may have a more pronounced effect on selectivity than the rate of heating. Paulik[5] elaborated the point about gas diffusion equilibrium established over the sample during heating. The controlled inert gas flow employed in this work prevented the establishment of such an equilibrium, thus facilitating the separation of the deaquation steps.

Another phenomenon which is clearly demonstrated in our special working conditions is the exothermic DTA peak accompanying the transformation of $NiSO_4 \cdot 7H_2O$ to $NiSO_4 \cdot 6H_2O$.

It was already observed that when the hexahydrate forms it melts in its own water[7]. The exothermic effect recorded between 35 and 85°C could be the net result of evaporation and solidification processes.

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