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## Note

# THERMAL PROPERTIES OF MAGNESIUM BISULPHITE HYDRAZINATE HYDRATE

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ABSTRACT

As part of our research programme on hydrazine hydrate–sulphur dioxide–metal ion systems, metal sulphite hydrazinate hydrates [1] $MSO_3xN_2H_4 \cdot yH_2O$, have been synthesized, where M = Fe, Mn, Co, Ni and Zn. The thermal properties of these complexes have also been studied. The synthesis and thermal properties of magnesium bisulphite hydrazinate hydrate is reported here for the first time; a literature survey on bisulphite hydrazinates did not find any previous mention of its synthesis.

## EXPERIMENTAL

Hydrazinium sulphite monohydrate, $(N_2H_5)_2SO_3 \cdot H_2O$, was prepared in situ by passing sulphur dioxide gas through alcoholic hydrazine hydrate. The colourless compound which separated out was filtered and washed with ether and dried in a vacuum over $P_2O_5$. An aqueous solution of $MgCl_2$ was mixed with aqueous $(N_2H_5)_2SO_3 \cdot H_2O$ (or $2N_2H_4 \cdot H_2SO_3 \cdot H_2O$) stoichiometrically with the ratio Mg : $SO_3$ equal to 1 : 2. The compound was precipitated out by addition of alcohol. It was then washed with alcohol, and then ether, and dried in a vacuum desiccator.

The composition of the Mg $(HSO_3)_2 \cdot N_2H_4 \cdot H_2O$ was demonstrated by chemical analysis. The magnesium content was determined by EDTA titration [2], hydrazine and sulphite (or sulphur) were analysed by a method described elsewhere [3]. Thermogravimetric experiments were carried out using a Stanton–Redcroft TG-750 thermobalance with 6–8 mg samples in nitrogen atmosphere. Differential thermal analysis (DTA) was carried out in air using an instrument described elsewhere [4], with 50–100 mg samples. The heating rate employed was 10 °C $min^{-1}$, both in TG and DTA.

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Platinum sample holders were used. Mass spectrometric analysis of the gaseous products of decomposition was carried out at the desired temperature in a vacuum ($10^{-8}$ torr) using an AEI MS-10 model instrument.

## RESULTS AND DISCUSSION

The alkaline earth metal, magnesium, forms $Mg(HSO_3)_2 \cdot N_2H_4 \cdot H_2O$, (found: Mg, 10.42; S, 26.9; $N_2H_4$, 13.62%; calculated: Mg, 10.29; S, 27.08; $N_2H_4$, 13.54%) which is readily soluble in water and is precipitated out by addition of alcohol.

$$2N_2H_4 \cdot H_2O + SO_2(g) \rightarrow (N_2H_5)_2SO_3 \cdot H_2O \quad (1)$$

$$(N_2H_5)_2SO_3 \cdot H_2O \rightleftharpoons (N_2H_4)_2 \cdot H_2SO_3 \cdot H_2O \quad (2)$$

$$MgCl_2 + 2(N_2H_4)_2 \cdot H_2SO_3 \cdot H_2O \rightarrow Mg(HSO_3)_2 \cdot N_2H_4 \cdot H_2O + HCl + N_2H_5Cl + H_2O + 2N_2H_4 \quad (3)$$

Interestingly, it was noticed that the same compound was obtained when synthesis was carried out with $(N_2H_5)_2SO_3 \cdot H_2O$ in hydrazine hydrate instead of aqueous solution.

The thermal studies of this colourless and highly hygroscopic compound, on heating upto 600°C, show three steps in the TG (Fig. 1). The first step with 16% weight loss is due to the loss of two water molecules which is

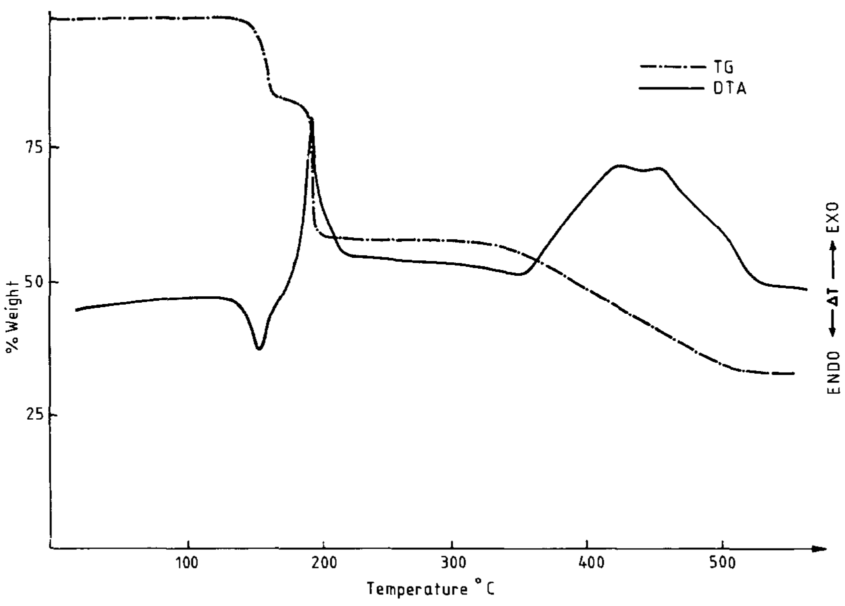


Fig. 1. TG and DTA of $Mg(HSO_3)_2 \cdot N_2H_4 \cdot H_2O$.

observed in the temperature range 133–160 °C. The bisulphite appears to dissociate [5] into $H_2O$ and $S_2O_5^{2-}$, accounting for one of the two $H_2O$ molecules. Thus

$$Mg(HSO_3)_2 \cdot N_2H_4 \cdot H_2O \xrightarrow{\Delta} MgS_2O_5 \cdot N_2H_4 + 2H_2O\uparrow \qquad (4)$$

Subsequently hydrazine decomposes at around 190 °C with the evolution of $N_2$ and $NH_3$ gases [6]. 41.5% weight loss is observed in the TG curve for this step.

$$3MgS_2O_5 \cdot N_2H_4 \rightarrow 3MgS_2O_3 + 3O_2\uparrow + 4NH_3\uparrow + N_2\uparrow \qquad (5)$$

The TG profile further shows the decomposition of the intermediate $MgS_2O_3$, magnesium thiosulphate, with a weight loss of 67.5% between 335 and 580 °C due to the formation of MgO and $MgSO_4$ by disproportionation.

$$MgS_2O_3 \rightleftharpoons MgSO_3 + S \qquad (6)$$

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (7)$$

$$SO_2 + 2MgSO_3 \rightarrow 2MgSO_4 + S \qquad (8)$$

Thus, $MgS_2O_3$ appears to form $MgSO_3$ before it undergoes disproportionation to oxide and sulphate as has been observed in the case of this sulphite by Okabe and Hori [7].

DTA shows an endotherm at 152 °C corresponding to the loss of $H_2O$. The two exotherms at 190 and 446 °C are complementary to the decomposition seen in the TG. The exotherm at 446 °C is broad and is probably due to the three reactions mentioned above for this step.

On heating in air, this compound exhibits the play of colour typical of the reaction

$$MgSO_3 + S \rightleftharpoons MgS_2O_3 \qquad (9)$$

Mass spectrometry of the evolved gases, after decomposition of the compound on heating to about 240 °C, was carried out. The gases $N_2$ $m/e = 14$, 28, $NH_3$ $m/e = 17$, $O_2$ $m/e = 16$ and $H_2O$ $m/e = 18$ were detected, thus supporting the proposed decomposition pattern.

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