

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] $\text{MSO}_3 \cdot x \text{N}_2\text{H}_4 \cdot y \text{H}_2\text{O}$, 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, $(\text{N}_2\text{H}_5)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, 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 $(\text{N}_2\text{H}_5)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ (or $2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_3 \cdot \text{H}_2\text{O}$) 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.

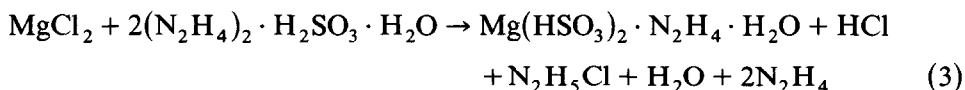
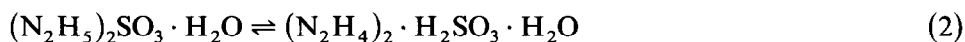
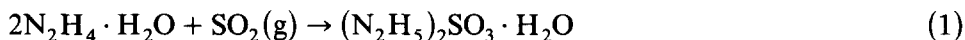
The composition of the $\text{Mg}(\text{HSO}_3)_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was demonstrated by chemical analysis. The magnesium content was determined by EDTA titration [2], hydrazine and sulphite (or sulphur) were analysed by a method described elsewhere [3]. Thermogravimetric 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 $10^\circ\text{C min}^{-1}$, 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 $\text{Mg}(\text{HSO}_3)_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, (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.



Interestingly, it was noticed that the same compound was obtained when synthesis was carried out with $(\text{N}_2\text{H}_5)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ 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

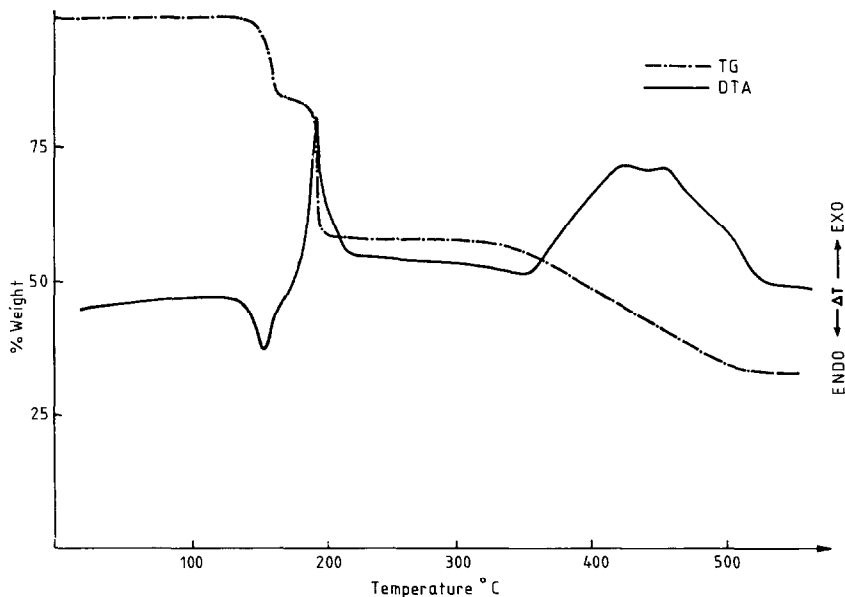
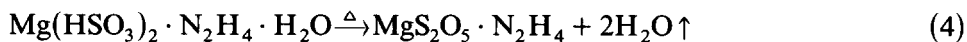
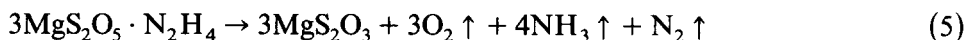


Fig. 1. TG and DTA of $\text{Mg}(\text{HSO}_3)_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

observed in the temperature range 133–160°C. The bisulphite appears to dissociate [5] into H₂O and S₂O₅²⁻, accounting for one of the two H₂O molecules. Thus



Subsequently hydrazine decomposes at around 190°C with the evolution of N₂ and NH₃ gases [6]. 41.5% weight loss is observed in the TG curve for this step.



The TG profile further shows the decomposition of the intermediate MgS₂O₃, magnesium thiosulphate, with a weight loss of 67.5% between 335 and 580°C due to the formation of MgO and MgSO₄ by disproportionation.



Thus, MgS₂O₃ appears to form MgSO₃ 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 H₂O. 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



Mass spectrometry of the evolved gases, after decomposition of the compound on heating to about 240°C, was carried out. The gases N₂ *m/e* = 14, 28, NH₃ *m/e* = 17, O₂ *m/e* = 16 and H₂O *m/e* = 18 were detected, thus supporting the proposed decomposition pattern.

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