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Note

THERMAL DECOMPOSITION OF HYDRAZINIUM ALUMINIUM SULFATE HYDRATE AND HYDRAZINATE

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As a part of our research programme on hydrazine derivatives [1–4], we have prepared a number of hydrazinium metal sulfates [1,5] $(N_2H_5)_2M(SO_4)_2$, where M = Mn, Fe, Co, Ni, Cu, Zn, Cd and Mg and their hydrazine adducts [2] of the type $(N_2H_5)_2M(SO_4)_2 \cdot 3N_2H_4$, where M = Fe, Co and Ni, as well as $N_2H_5Al(SO_4)_2 \cdot 6N_2H_4$. Recently, we reported [5,6] the thermal analysis of these compounds. Our literature survey on the thermal analysis of alums [7] and aluminium salts [8] indicated that, although the preparation of hydrazinium aluminium sulfate dodecahydrate, $N_2H_5Al(SO_4)_2 \cdot 12H_2O$, has been reported [9], there appears to be no report on its thermal analysis. Here, we report the results of the thermal analysis of $N_2H_5Al(SO_4)_2 \cdot 12\ H_2O$ and $N_2H_5Al(SO_4)_2 \cdot 2N_2H_4$.

EXPERIMENTAL

Hydrazinium aluminium sulfate dodecahydrate, $N_2H_5Al(SO_4)_2 \cdot 12\ H_2O$, was prepared by a modified method described earlier [2]. In this procedure, we have produced hydrazinium sulfate in situ by dissolving ammonium sulfate in hydrazine hydrate [3]. The composition was fixed by chemical analysis (found: Al 5.59, N_2H_4 6.60, SO_4^{2-} 40.80%; calcd: Al 5.77, N_2H_4 6.84, SO_4^{2-} 41.04%) and the reaction can be written as

$$(NH_4)_2SO_4 + 2N_2H_4 \cdot H_2O \rightarrow (N_2H_5)_2SO_4 + 2NH_3 + 2H_2O \quad (1)$$

$$(N_2H_5)_2SO_4(aq) + Al_2(SO_4)_3 \cdot 18\ H_2O\ (aq) + 6\ H_2O \rightarrow 2N_2H_5Al(SO_4)_2 \cdot 12\ H_2O \quad (2)$$

Hydrazinium aluminium sulfate dihydrazinate, $N_2H_5Al(SO_4)_2 \cdot 2N_2H_4$, was prepared by treating ammonium aluminium sulfate dodecahydrate, $NH_4Al(SO_4)_2 \cdot 12\ H_2O$, with excess of hydrazine hydrate (99–100%) as reported [3]. The hexahydrazinate, $N_2H_5Al(SO_4)_2 \cdot 6N_2H_4$, formed initially is unstable and loses four hydrazine molecules at room temperature to give a

stable dihydrazinate (found: Al 8.33, N_2H_4 29.67, SO_4^{2-} 60.50%; calcd: Al 8.58, N_2H_4 30.38, SO_4^{2-} 61.04%).

The compositions of both $N_2H_5Al(SO_4)_2 \cdot 12\ H_2O$ and $N_2H_5Al(SO_4)_2 \cdot 2\ N_2H_4$ were fixed by chemical analysis. The aluminium content was fixed by EDTA titration, hydrazine was determined by titration with 0.025 M KIO_3 under Andrew's conditions [3] and sulfate was estimated gravimetrically as $BaSO_4$. Thermogravimetric (TG) experiments were carried out using a Stanton-Redcroft TG-750 thermobalance with 6–8 mg samples. Differential thermal analysis (DTA) was carried out using an instrument described elsewhere [10] with 50–100 mg samples. The heating rate employed was 10°C min^{-1} both in TG and DTA. Platinum sample holders were used. A nitrogen atmosphere was used during the TG experiments and the DTA experiments were carried out in air.

RESULTS AND DISCUSSION

Thermal decomposition of hydrazinium aluminium sulfate dodecahydrate

The DTA curve for $N_2H_5Al(SO_4)_2 \cdot 12\ H_2O$ (Fig. 1) shows four endothermic peaks at 76, 88, 135 and 890°C and an exothermic peak at 280°C. The endothermic peak at 76°C is due to the dissolution of hydrazinium aluminium sulfate in the water of crystallisation, although part of the water is removed during the reaction. The endothermic peaks at 88 and 135°C are ascribed to dehydration of $N_2H_5Al(SO_4)_2 \cdot 12\ H_2O$ to $N_2H_5Al(SO_4)_2 \cdot 6\ H_2O$ and of $N_2H_5Al(SO_4)_2 \cdot 6\ H_2O$ to anhydrous $N_2H_5Al(SO_4)_2$, respectively. The exothermic reaction at 280°C is due to the decomposition of anhydrous

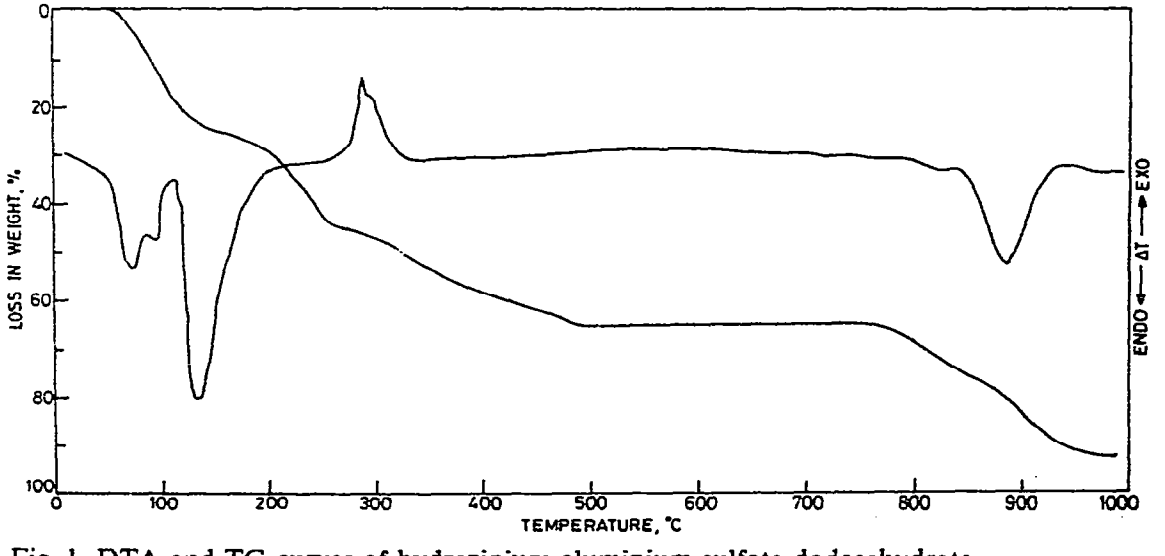

Fig. 1. DTA and TG curves of hydrazinium aluminium sulfate dodecahydrate.

$N_2H_5Al(SO_4)_2$ to anhydrous aluminium sulfate. The broad endothermic reaction at 890°C, in which the reaction occurs in the temperature range 830–940°C, arises from the decomposition of anhydrous aluminium sulfate to alumina. This explanation is supported by the TG curve (Fig. 1) and the reaction can be written as

$$N_2H_5Al(SO_4)_2 \cdot 12\,H_2O \xrightarrow[88°C\ (endo)]{55-120°C} N_2H_5Al(SO_4)_2 \cdot 6\,H_2O + 6\,H_2O \quad (3)$$

$$N_2H_5Al(SO_4)_2 \cdot 6\,H_2O \xrightarrow[135°C\ (endo)]{120-255°C} N_2H_5Al(SO_4)_2 + 6\,H_2O \quad (4)$$

$$2\,N_2H_5Al(SO_4)_2 \xrightarrow[280°C\ (exo)]{255-495°C} Al_2(SO_4)_3 + (N_2H_5)_2SO_4 \quad (5)$$

$$Al_2(SO_4)_3 \xrightarrow[890°C\ (endo)]{740-965°C} Al_2O_3 + 3\,SO_2 + \tfrac{3}{2}\,O_2 \quad (6)$$

Thermal decomposition of hydrazinium aluminium sulfate dihydrazinate

The DTA curve for $N_2H_5Al(SO_4)_2 \cdot 2\,N_2H_4$ (Fig. 2) shows two exothermic peaks at 200 and 270°C and an endothermic peak at 870°C. The exothermic reaction centred around 200°C is due to the dehydrazination of $N_2H_5Al(SO_4)_2 \cdot 2\,N_2H_4$ to $N_2H_5Al(SO_4)_2$ which further decomposes as above. This is supported by the TG curve (Fig. 2) and the reaction can be written as

$$N_2H_5Al(SO_4)_2 \cdot 2\,N_2H_4 \xrightarrow[200°C\ (exo)]{110-260°C} N_2H_5Al(SO_4)_2 + 2\,N_2H_4 \quad (7)$$

The weight loss observed during TG (Table 1) is in good agreement with the expected value for the various steps in both the compounds.

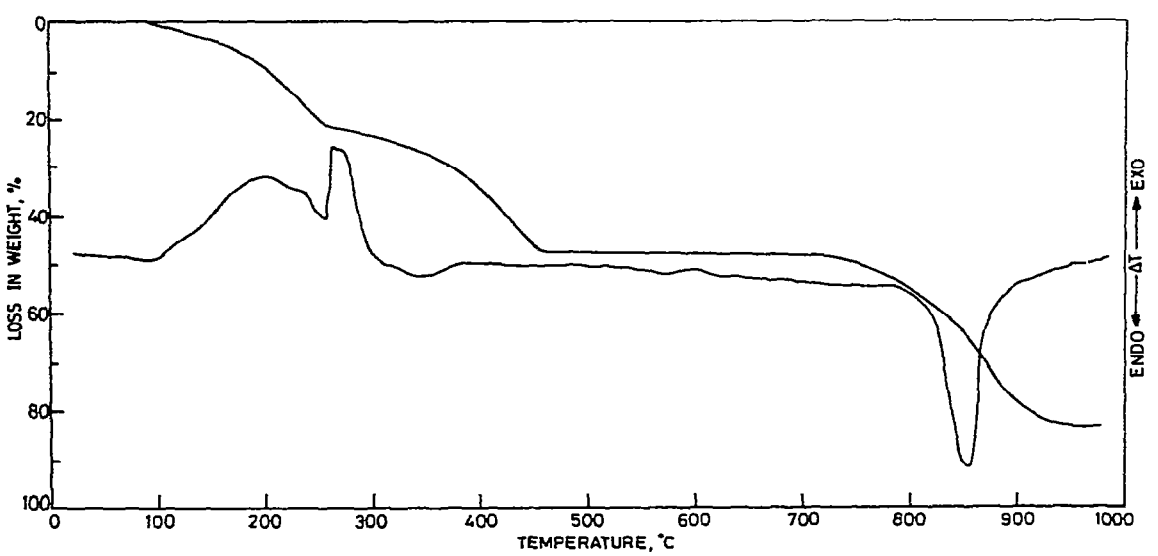

Fig. 2. DTA and TG curves of hydrazinium aluminium sulfate dihydrazinate.

TABLE 1

Thermal data of $N_2H_5Al(SO_4)_2 \cdot 12\ H_2O$ and $N_2H_5Al(SO_4)_2 \cdot 2\ N_2H_4$

Compound	Step No.	Thermogravimetry			DTA peak temp. (°C)	Reaction (equation number)
		Temp. range (°C)	Total Wt. loss (%)			
			Obsd.	Reqd.		
$N_2H_5Al(SO_4)_2 \cdot 12\ H_2O$	1	55–120	22.80	23.07	88 (endo)	3
	2	120–255	45.10	46.14	135 (endo)	4
	3	255–495	63.00	63.45	280 (exo)	5
	4	740–965	90.00	89.11	890 (endo)	6
$N_2H_5Al(SO_4)_2 \cdot 2\ N_2H_4$	1	110–260	21.10	20.25	200 (exo)	7
	2	260–465	46.50	45.89	270 (exo)	5
	3	725–940	83.20	83.87	870 (endo)	6

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