

## **SYNTHESES AND THERMAL DECOMPOSITIONS OF HYDRAZINIUM SALTS**

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Hydrazinium salts, such as the sulfate monohydrate, picrate hemihydrate, monobasic phosphate and dibasic phosphate, have been prepared by the reactions of the corresponding ammonium salts with hydrazine hydrate. The thermal properties of these hydrazinium salts have been investigated using differential thermal analysis and thermogravimetry.

Recently in our laboratory the reaction between hydrazine hydrate and ammonium salts was found to be a suitable and simple method for the preparation of hydrazinium salts [1,2] such as  $N_2H_5HF_2$  [3],  $N_2H_5VO_3$  [4] and  $N_2H_5HSO_4$  [5], which could not be prepared by any other method. The thermal behaviour of the hydrazinium salts prepared has been investigated [2–6]. In a continuation of our studies on hydrazinium salts, we have now prepared some more salts: dihydrazinium sulfate monohydrate, hydrazinium picrate hemihydrate, monohydrazinium phosphate and dihydrazinium phosphate. The thermal decompositions of these salts have been studied using DTA and TG. The reaction between  $NH_4IO_3$  and  $N_2H_4 \cdot H_2O$  is also reported which resulted in ignition.

### **Experimental**

#### *Materials*

Hydrazine hydrate was a 99–100% pure commercial sample, BDH. All the ammonium salts used in this study were guaranteed samples.

#### *Synthesis of hydrazinium salts*

The hydrazinium salts were prepared as described before [1–4]. Dihydrazinium sulfate monohydrate,  $(N_2H_5)_2SO_4 \cdot H_2O$ , was obtained by crystallizing the salt over anhydrous calcium chloride.

#### *Analyses*

The hydrazine contents of the hydrazinium salts were determined by a standard volumetric method, using  $KIO_3$  [7]. The water contents present as hydrates were determined via the TG weight loss at 80–150°.

### *IR spectra*

The IR spectra of the salts were recorded with a Carl-Zeiss UR-10 double beam spectrophotometer, using KBr pellets, in the region  $4000\text{--}400\text{ cm}^{-1}$

### *Differential thermal analysis*

The DTA curves of the hydrazinium salts were recorded using a home-made DTA unit, as described elsewhere [8]. The DTA experiments were performed in air at a heating rate of  $10\text{ deg. min}^{-1}$ . About 100 mg powdered samples was used, with close packing.

### *Thermogravimetry*

TG was carried out using a Stanton Redcroft 750/770 thermobalance. The heating rate employed was  $10\text{ deg. min}^{-1}$  in air. About 7 mg sample was used for each experiment.

## **Results and discussion**

The reactions of the solid ammonium salts  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{NH}_4\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{HPO}_4$  with hydrazine hydrate yielded the corresponding hydrazinium salts. However, the reaction between  $\text{NH}_4\text{IO}_3$  and  $\text{N}_2\text{H}_4\text{H}_2\text{O}$  was violent, and ignition took place with the evolution of violet iodine vapor, ammonia etc. even at  $0^\circ$ . From the evolution of ammonia gas and the delay in the liberation of iodine vapor, it is suggested that hydrazinium iodate,  $\text{N}_2\text{H}_5\text{IO}_3$ , might be formed first as an unstable intermediate, which decomposes due to the strong oxidizing property of iodate.

Hydrazinium picrate hemihydrate is a non-hygroscopic yellow crystalline material and all the other three hydrazinium salts are hygroscopic solids. The results of chemical analyses, the melting points and the  $\nu_{\text{N-N}}$  of the hydrazinium salts are given in Table 1. The  $\nu_{\text{N-N}}$  frequencies in the region  $960\text{--}980\text{ cm}^{-1}$  suggest the presence of  $\text{N}_2\text{H}_5^+$  ion in all these salts [9,10]. The results of the thermal decompositions of these salts are given in Table 2 and are discussed below.

### *Dihydrazinium sulfate monohydrate, $(\text{N}_2\text{H}_5)_2\text{SO}_4\cdot\text{H}_2\text{O}$*

The preparation of this salt was reported as early as 1916 by Summer and Weise [11], by the reaction of  $\text{N}_2\text{H}_6\text{SO}_4$  with an excess of  $\text{BaCO}_3$ . The DTA of anhydrous  $(\text{N}_2\text{H}_5)_2\text{SO}_4$  has been reported [6] and the behaviour of  $(\text{N}_2\text{H}_5)_2\text{SO}_4$  towards heat was studied by Turrentine [12]. The decomposition products, however, have not been fully investigated. It is therefore of interest to study the thermal decomposition behaviour of  $(\text{N}_2\text{H}_5)_2\text{SO}_4\cdot\text{H}_2\text{O}$ .

The TG and DTA curves of  $(\text{N}_2\text{H}_5)_2\text{SO}_4\cdot\text{H}_2\text{O}$  are shown in Fig. 1a. The salt melts with dehydration, which corresponds to the endotherm at  $56^\circ$  in the DTA curve and a