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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 $N_2H_4.H_2O$ 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, $(N_2H_5)_2SO_4.H_2O$, 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 4000–400 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 $deg.min^{-1}$. 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 deg. min^{-1} in air. About 7 mg sample was used for each experiment.

Results and discussion

The reactions of the solid ammonium salts $NH_4H_2PO_4$, $NH_4C_6H_2(NO_2)_3O$, $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ with hydrazine hydrate yielded the corresponding hydrazinium salts. However, the reaction between NH_4IO_3 and $N_2H_4H_2O$ was violent, and ignition took place with the evolution of violet iodine vapor, ammonia etc. even at 0^o. From the evolution of ammonia gas and the delay in the liberation of iodine vapor, it is suggested that hydrazinium iodate, $N_2H_5IO_3$, 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 ν_{N-N} of the hydrazinium salts are given in Table 1. The ν_{N-N} frequencies in the region 960–980 cm^{-1} suggest the presence of $N_2H_5^+$ 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, $(N_2H_5)_2SO_4.H_2O$

The preparation of this salt was reported as early as 1916 by Summer and Weise [11], by the reaction of $N_2H_6SO_4$ with an excess of $BaCO_3$. The DTA of anhydrous $(N_2H_5)_2SO_4$ has been reported [6] and the behaviour of $(N_2H_5)_2SO_4$ 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 $(N_2H_5)_2SO_4.H_2O$.

The TG and DTA curves of $(N_2H_5)_2SO_4.H_2O$ are shown in Fig. 1a. The salt melts with dehydration, which corresponds to the endotherm at 56^o in the DTA curve and a

Table 1 Analytical data on hydrazinium salts

Hydrazinium salt	Melting point, °C	% N_2H_4 obsd.	(calcd.)	$\nu_{N-N'}$ cm^{-1}
$(N_2H_5)_2SO_4.H_2O$	48–49	34.87	(35.58)	964
$N_2H_5C_6H_2(NO_2)_3O.1/2H_2O$	160(d)	11.80	(11.86)	983
$N_2H_5H_2PO_4$	83	24.39	(24.62)	967
$(N_2H_5)_2HPO_4$	114-116	39.58	(39.54)	966

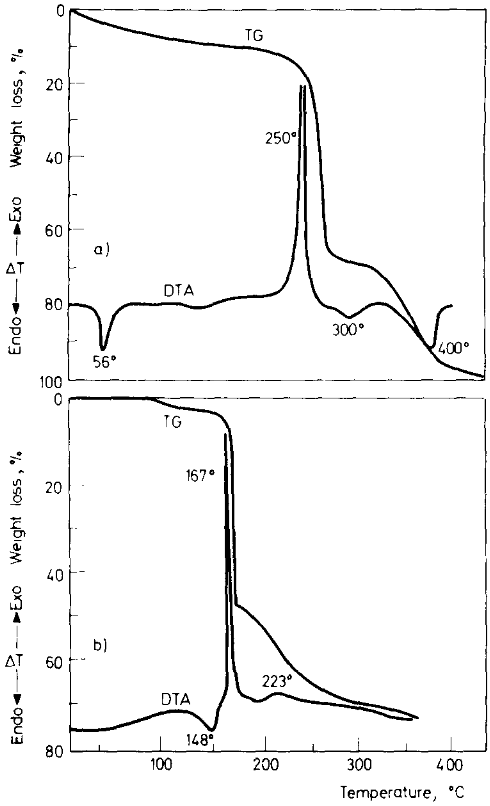

Fig. 1. DTA and TG curves of
a) dihydrazinium sulfate monohydrate and
b) hydrazinium picrate hemihydrate

10% weight loss in the TG curve (weight loss expected for dehydration 10.0%). The TG curve shows that the decomposition of $(N_2H_5)_2SO_4$ commences very slowly at 170°, and a sudden weight loss occurs in the range 250–280°. The gaseous products of decomposition of $(N_2H_5)_2SO_4$, as found by qualitative analysis, are SO_2, H_2S, NH_3 and S. The residue left behind after the exotherm was found to be a mixture of ammonium sulfate and ammonium bisulfate. The ammonium sulfate present in the mixture decomposes to ammonium bisulfate, which further decomposes and volatilizes. The endotherms at 300° and 398° are characteristic of the decompositions of ammonium sulfate and ammonium bisulfate, respectively [13,14]. On the basis of the weight loss observed in the TG curve and the qualitative analyses of the products of decomposition, the probable equations for the thermal decomposition of dihydrazinium sulfate monohydrate are given in Table 2.

Hydrazinium picrate hemihydrate, $N_2H_5C_6H_2(NO_2)_3O.1/2H_2O$

The thermal decompositions of picric acid and picrates have been studied in detail [15,16]. Under certain circumstances, the salts of picric acid, and in particular ammonium picrate and picric acid, are well-known explosives [17]. Hydrazinium picrate has also been classified as an explosive [18], even though the oxidizer to fuel ratio is as low as 0.45. There are only two reports on the thermal decomposition of hydrazinium picrate hemihydrate [19,20]. Fauth reported [19] that the salt detonates at 105°. According to Datta and Chatterjee [20] the salt melts at 201° and explodes at 385°. Because of the inconsistency in the decomposition temperature of hydrozinium picrate hemihydrate reported by these authors, it was thought necessary to reinvestigate the thermal decomposition of the salt. Here, the preliminary results of DTA and TG are given.

The TG and DTA curves of hydrazinium picrate hemihydrate (particle size 75–100 μm) are shown in Fig. 1b. The endotherm at 148° in the DTA curve may be attributed to dehydration, since correspondingly the TG curve shows a 2.9% weight loss against 3.3% for the loss of half a molecule of water. The exotherm at 167° is due to the decomposition of the salt, probably to carbonaceous matter, which is further oxidized in air. Thus, the small exotherm at 223° may be attributed to this oxidation. During the decomposition at 167°, part of the hydrazinium picrate sublimes, as seen from the yellow deposit of the salt on the sides of the lid in the furnace and the hydrazine content present in the deposit. The exothermic peak at 167° seems to be sensitive to the atmosphere, since the exothermic peak is shifted to 198° in nitrogen atmosphere.

Monohydrazinium phosphate, $N_2H_5H_2PO_4$

The hydrazinium phosphates $N_2H_5H_2PO_4$ and $(N_2H_5)_2HPO_4$ have been investigated as flame retardants in cellulosic materials [21]. However, the thermal decompositions of these salts were not discussed in detail.

Table 2 DTA and TG results for the hydrazinium salts

Hydrazine salt	DTA peak temp., °C	Thermogravimetry		Phenomena
		Temp. range, °C	Weight loss obsd., %	
$(N_2H_5)_2SO_4.H_2O$	56(−)	32-150	10.0	melting and dehydration
	259(+)	170-280	67.5	$10(N_2H_5)_2SO_4 \rightarrow 2(NH_4)_2SO_4+3NH_4HSO_4+18H_2O+S+3H_2S+SO_2+12N_2+9NH_3$
	300(−)			
	398(−)	300-430		$(NH_4)_2SO_4 \rightarrow NH_4HSO_4+NH_3$ decomp. and volatilization of NH_4HSO_4
$N_2H_5C_6H_2(NO_2)_3O.1/2H_2O$	148(−)	90-135	2.9	dehydration
	167(+)	160-180	48.0	decomposition of the salt, probably to carbonaceous matter
	223(+)	185-350	74.0	partial oxidation of char
$N_2H_5H_2PO_4$	83(−)	-	-	melting
	107(−)	80-110	7.5	$2N_2H_5H_2PO_4 \rightarrow (N_2H_5)_2H_2P_2O_7+H_2O$
	119(−)	115-125	12.8	$(N_2H_5)_2H_2P_2O_7 \rightarrow 2N_2H_5PO_3+H_2O$
	190(−)	130-215	25.5	$2N_2H_5PO_3 \rightarrow N_2H_5HP_2O_6+N_2H_4$
	266(+)	220-320	42.0	$2N_2H_5HP_2O_6 \rightarrow 2HPO_3$+gases such as ammonia, etc.
$(N_2H_5)_2HPO_4$	125(−)	-	-	melting
	156(−)	130-165	14.0	$2(N_2H_5)_2HPO_4 \rightarrow (N_2H_5)_3HP_2O_7+N_2H_4+H_2O$
	187(−)	165-250	41.0	$(N_2H_5)_3HP_2O_7 \rightarrow N_2H_5HP_2O_6+N_2H_4+H_2O$
	266(+)	250-450	50.0	$N_2H_5HP_2O_6 \rightarrow 2HPO_3$+gases such as ammonia, etc.

(+) exotherm and (−) endotherm

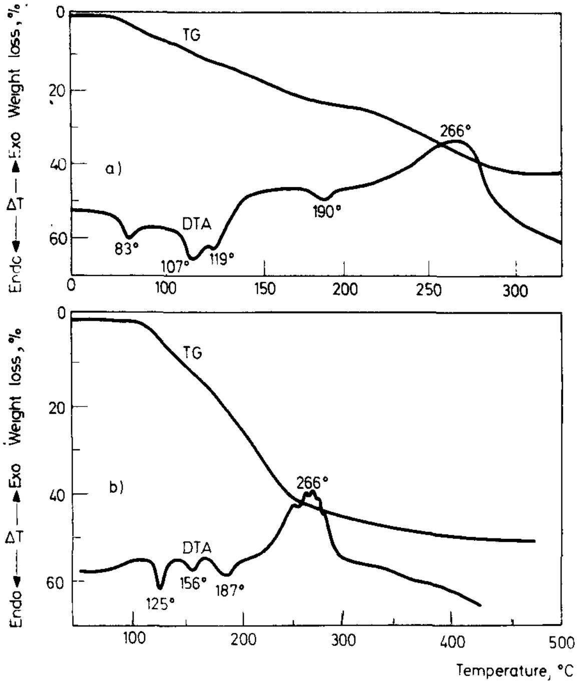

Fig. 2. DTA and TG curves of
a) monohydrazinium phosphate
and b) dihydrazinium phosphate

The TG and DTA curves of $N_2H_5H_2PO_4$ are shown in Fig. 2a. The first endotherm, at 83°, is due to the melting of the salt. The endotherms at 107° and 119° are attributed to dehydration. On the basis of the TG weight loss (obsd. 7.5% and calcd. 6.9%), the intermediate formed at the endotherm at 107° is proposed to be dihydrazinium pyrophosphate, $(N_2H_5)_2H_2P_2O_7$. Further, the compound $(N_2H_5)_2H_2P_2O_7$ loses one molecule of water to form hydrazinium metaphosphate, $N_2H_5PO_3$. The endotherm at 119° corresponds to the loss of one water molecule and the formation of $N_2H_5PO_3$. The weight loss observed (12.8%) in the TG curve is in good agreement with the calculated loss of weight, 13.8%. The corresponding ammonium salt, $NH_4H_2PO_4$, is reported [22] to form similar intermediates, such as $(NH_4)_2H_2P_2O_7$, NH_4PO_3, etc. The salt $N_2H_5PO_3$ further decomposes to $N_2H_4.2HPO_3$ or $N_2H_6P_2O_6$ in the range 130–215°, as observed in the TG curve (Table 2) with an observed weight loss of 25.5% (required 26.2%). This corresponds to a weak endotherm at 190° in the DTA curve. The exotherm at 266° in the DTA curve has been attributed to the formation of a syrupy liquid, metaphosphoric acid (TG weight loss observed 42.0% and calcd. 39.4%). The thermal decomposition of $N_2H_5H_2PO_4$ is quite similar to that of the ammonium salt, $NH_4H_2PO_4$ [15,22–24].

Dihydrazinium phosphate, $(N_2H_5)_2HPO_4$

The DTA and TG curves of dihydrazinium phosphate are given in Fig. 2b. The salt melts at 114–116° in the melting-point apparatus (Table 1). The first endotherm, at 125°, is therefore due to the melting of $(N_2H_5)_2HPO_4$. The endotherm at 156° is attributed to dehydration and dehydrazination. The TG shows a weight loss of ~ 14% against the calculated weight loss of 15.4% for the formation of the intermediate $(N_2H_5)_3HP_2O_7$ (Table 2). The formation of the proposed intermediate is supported by the observed hydrazine content (34.1%) of the residue obtained after the endotherm at 156° (calcd. 35.1%). The residue further loses weight continuously. The endotherm at 187° has been attributed to dehydration and dehydrazination with the formation of the compound $N_2H_6P_2O_6$ or $N_2H_4.2HPO_3$. This intermediate $N_2H_4.2HPO_3$ is similar to that proposed for the endotherm at 190° during the thermal decomposition of $N_2H_5H_2PO_4$. The proposed intermediate finds support from the TG weight loss (obsd. 41.0% and calcd. 40.7%) and the hydrazine content estimated for the residue obtained at 240° (obsd. 18.2% and calcd. 16.6%). The exotherm at 266° in the DTA curve is attributed to the decomposition of $N_2H_4.2HPO_3$ to metaphosphoric acid, HPO_3. The TG curve also shows a weight loss of 50% required for the formation of HPO_3 (calcd. 50.6%). It appears from the thermal decompositions of $N_2H_5H_2PO_4$ and $(N_2H_5)_2HPO_4$ that both the salts decompose through the intermediate $N_2H_4.2HPO_3$ to metaphosphoric acid. Similar thermal decompositions leading to continuous dehydration with the formation of various polyphosphoric acid salts have been reported in the literature [15,22–24] for the thermal decompositions of mono- and diammonium phosphates. Further, a number of hydrazine salts of polyphosphoric acids have also been reported [25–28].

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Zusammenfassung — Hydraziniumsalze wie Hydraziniumsulfat-Monohydrat, Hydraziniumpikrat-Semihydrat sowie mono- und dibasisches Phosphat wurden durch Umsetzung der entsprechenden Ammoniumsalze mit Hydrazinhydrat hergestellt. Die thermischen Eigenschaften dieser Hydraziniumsalze wurden differential thermoanalytisch und thermogravimetrisch untersucht.

Резюме — Получены моногидрат сульфата-, полугидрат пикрата-, первичный фосфат- и вторичный фосфат гидразония, реакцией соответствующей аммонийной солис гидразин гидратом. Термические свойства этих солей были исследованы методами ДТА и ТГ.