

Preparation, characterisation and thermal properties of hydrazinium derivatives. Part III

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Abstract. Hydrazinium acetate, metavanadate, sulfite, sulphamate and thiocyanate have been prepared by the reaction of corresponding ammonium salts with hydrazine hydrate. The compounds were characterised by chemical analysis and infrared spectra. Thermal behaviour of these hydrazinium derivatives have been investigated using thermogravimetry and differential thermal analysis.

Keywords. Hydrazinium salts ; thermal analysis.

1. Introduction

Recently we reported the preparation and characterisation of a number of hydrazinium derivatives by the reaction of solid ammonium salts with hydrazine hydrate (Patil *et al* 1978, 1979a). Differential thermal analysis of a number of hydrazinium derivatives have also been discussed (Patil *et al* 1979b). In continuation of our studies on hydrazinium salts we have now prepared some more compounds and studied their thermal behaviour using thermogravimetry and differential thermal analysis.

2. Experimental

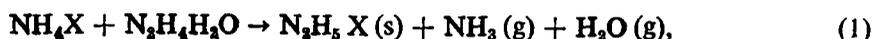
All the ammonium salts used were of analytical grade. Hydrazine hydrate (99-100 %) was a BDH product. Stoichiometric quantities of an ammonium salt and hydrazine hydrate were mixed when homogeneous solution was obtained with the evolution of ammonia indicating that the reaction was instantaneous. The resulting solution was allowed to crystallise in a vacuum desiccator over phosphorous pentoxide. In all the cases the conversion of ammonium salt to hydrazinium salt was quantitative.

The hydrazine content in the hydrazinium salts was estimated volumetrically using potassium iodate solution (0.05 M) under Andrews conditions (Vogel 1951). In hydrazinium thiocyanate and hydrazinium metavanadate it was not possible

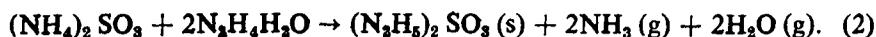
to estimate the hydrazine content by this method since both the thiocyanate and the metavanadate also reacted with potassium iodate. The percentage of thiocyanate in hydrazinium thiocyanate was determined gravimetrically as CuSCN (Vittal *et al* 1979). The vanadate content in hydrazinium metavanadate was determined by thermally decomposing $N_2H_5VO_3$ around $500^\circ C$ and weighing the residue as V_2O_5 . Infrared spectra of the compounds were recorded using Carl Zeiss UR-10 spectrophotometer as KBr pellets. The infrared spectrum of hydrazinium sulphamate was taken as neat. Differential thermal analysis (DTA) was carried out on an automatic recording DTA-02 Universal Instrument manufactured by Franz-Wagner Industrielle Elektronik of GDR using about 20 mg of the sample. The heating rate employed was $7^\circ C/min$. Thermogravimetric (TG) experiments were carried out with Stanton Redcroft TG-750 Thermobalance using 6-8 mg of the sample with a heating rate of $5^\circ C/min$. All the DTA and TG experiments were done in air.

3. Results and discussion

The reaction of solid ammonium salts with hydrazine hydrate yields the corresponding hydrazinium salts as reported earlier. The reaction is quantitative.



where $X = CH_3COO, SCN, SO_3NH_2$ and VO_3 ,



All the hydrazinium salts prepared are hygroscopic white solids, the exceptions being hydrazinium metavanadate which is a brown amorphous solid and hydrazinium sulphamate which is a colourless liquid. The results of chemical analysis, melting points and IR are given in table 1. All compounds show IR absorption of ν_{N-N} characteristic of $N_2H_5^+$ around $960-980\text{ cm}^{-1}$ (Braibanti *et al* 1968).

Table 1. Analytical data of hydrazinium derivatives.

No.	Compound	Melting point ($^\circ C$)		% Hydrazine		IR absorption $\nu_{N-N}\text{ cm}^{-1}$
		Observed	Reported	Observed	Theoretical	
1.	$N_2H_5COOCH_3$	96-98	97	35.49	34.78	980
2.	$N_2H_5VO_3$	d	..	24.23*	24.24*	960
				% VO_3 (75.05)	(74.96)	
3.	$(N_2H_5)_2SO_3$	71-73	..	43.96	43.71	980
4.	$(N_2H_5)_2SO_3 \cdot H_2O$	45-46	..	38.97	39.02	980
5.	N_2H_5SCN	78-79	77.5	35.00*	35.16*	980
				% SCN (63.92)	(63.93)	
6.	$N_2H_5SO_3NH_2$	d	..	23.43	24.80	980

* Hydrazine content was determined indirectly by estimating the corresponding anion, the percentage of which is given in brackets.

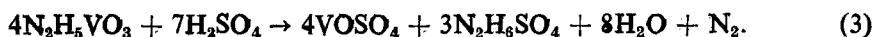
3.1. Hydrazinium acetate ($N_2H_5COOCH_3$)

TG and DTA curves of $N_2H_5COOCH_3$ are shown in figure 1a. DTA shows two endotherms. The first endothermic peak at $105^\circ C$ is due to the melting of the compound which agrees with the reported value (Hady *et al* 1969). The second endotherm at $175^\circ C$ is assigned to the decomposition of the melt into gaseous products containing acetic acid and ammonia as found by the qualitative test of the gaseous products. The TG shows a single-step decomposition starting around $75^\circ C$ and ending near $200^\circ C$. The results of TG and DTA are complementary to each other.

3.2. Hydrazinium metavanadate ($N_2H_5VO_3$)

Our earlier attempts to prepare $N_2H_5CrO_4$ and $(N_2H_5)_2Cr_2O_7$ by the reaction of corresponding ammonium salts with hydrazine hydrate were not successful due to their strong oxidising properties. However, we could obtain hydrazinium metavanadate, $N_2H_5VO_3$ when hydrazine hydrate was added to solid ammonium metavanadate, NH_4VO_3 at $0^\circ C$. The analysis of the product showed only 14.20% N_2H_4 against 24.28% N_2H_4 required for the formula. However, the amount VO_3^- determined by gravimetric analysis is in good agreement (table 1). The discrepancy in the hydrazine content determined by the volumetric analysis of $N_2H_5VO_3$ has been attributed to the side reaction, where some of the $N_2H_5^+$ ions are utilised for the reduction of V^V to V^{IV} . Formation of $N_2H_5VO_3$ was further confirmed by the infrared spectrum of the compound. The characteristic IR absorption of ν_{N-N} of N_2H_5 is observed at 960^{-1} . The IR absorption frequencies of VO_3^- are seen at 870 (vs) and 760 (vs) cm^{-1} .

The reaction of $N_2H_5VO_3$ with concentrated H_2SO_4 gave vanadyl sulphate, $VOSO_4$ and hydrazine sulphate, $N_2H_6SO_4$. The reaction can be written as:



Formation of $VOSO_4$ was confirmed by the blue colour of the solution and UV visible spectra. Hydrazine sulfate which precipitates as a white solid was charac-

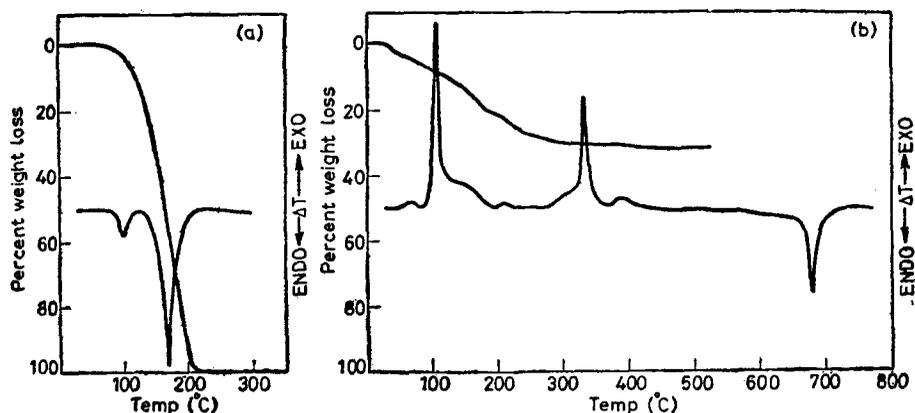


Figure 1. DTA and TG of (a) hydrazinium acetate, $N_2H_5COOCH_3$; (b) hydrazinium metavanadate, $N_2H_5VO_3$.

terised by its melting point and hydrazine content. Further, the amount of $N_2H_6SO_4$ formed was determined quantitatively by reacting a known amount of $N_2H_5VO_3$ (1 g) with concentrated H_2SO_4 . In a typical experiment the amount of $N_2H_6SO_4$ formed was 0.60 g. This is rather too low a value compared to the expected value of 0.74 g for the reaction (3). This discrepancy could be due to the dual nature of the hydrazine which behaves as one-electron and four-electron-reductant (Audrieth and Ogg 1951; Krishna Rao and Gopal Rao 1973).

The TG and DTA curves of $N_2H_5VO_3$ are shown in figure 1b. As can be seen from the TG curve, it is highly unstable and starts decomposing from the room temperature. The DTA shows two exotherms at 104° C and 330° C followed by an endotherm at 680° C. The first exotherm at 104° C is probably due to the oxidation of hydrazine leaving a black residue which decomposes to vanadium pentoxide. The appearance of 330° C exotherm is not clear. However, the residue after the exotherm 330° C was identified as V_2O_5 by weight loss in TG as well by the endotherm at 680° C in DTA which is due to the melting of V_2O_5 .

3.3. Hydrazinium sulphite monohydrate ($(N_2H_5)_2SO_3 \cdot H_2O$)

The DTA and TG curves of $(N_2H_5)_2SO_3 \cdot H_2O$ are shown in figure 2a. The DTA shows an endothermic peak at 52° C (Melting). The second endotherm near 100° C is attributed to the dehydration. The anhydrous salt $(N_2H_5)_2SO_3$ decomposes exothermically at 276° C. The TG shows a three-step decomposition. The first step is due to dehydration (percentage weight loss; observed 10.00; calculated 10.94). The second step is due to the decomposition of the anhydrous salt with a weight loss about 65%. It was not possible to fix the composition of the residue at this stage. The qualitative analysis of the residue obtained by heating $(N_2H_5)_2SO_3 \cdot H_2O$ isothermally at 275° C gave tests for NH_4^+ , SO_4^{2-} , $S_2O_3^{2-}$ and polysulphide. It is possible that $(N_2H_5)_2SO_3$ decomposes exothermically giving sulphur which probably reacts with undecomposed SO_3^{2-} in the melt to give $S_2O_3^{2-}$. The final step (100% weight loss) has been assigned to the decomposition and volatilisation of the products. There is good agreement in the TG and DTA results.

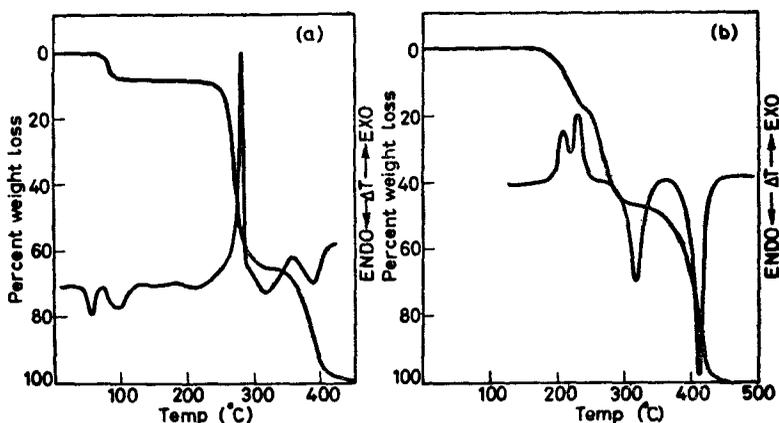


Figure 2. DTA and TG of (a) hydrazinium sulfite monohydrate, $(N_2H_5)_2SO_3 \cdot H_2O$; (b) hydrazinium sulfamate, $N_2H_5SO_3NH_2$.

3.4. Hydrazinium sulphamate ($N_2H_5SO_3NH_2$)

The TG and DTA curves of $N_2H_5SO_3NH_2$ are shown in figure 2b. The DTA shows two exotherms at 212 and 237° C and two endotherms at 317 and 410° C respectively. The TG exhibits a two-step decomposition corresponding to the two exotherms and a single-step corresponding to the two endotherms. The liquid $N_2H_5SO_3NH_2$ slowly loses ammonia initially, then decomposes exothermically and vigorously, forming a white solid with the evolution of NH_3 , H_2O , SO_2 and S, etc., which were detected by qualitative analysis. The TG shows that the compound starts decomposing from 190° C with a little break around 215° C. The white solid formed with about 47% weight loss was found to be acidic (pH \approx 2), gave effervescence with $NaHCO_3$ solution and showed test for ammonium ion.

Hydrazinium sulphamate initially decomposes to give sulphamic acid which appears to decompose instantaneously due to the exothermicity of the first reaction. This acidic residue may be $HN(SO_3NH_4)_2$ or $NH_4N(SO_3H)_2$ similar to the intermediate formed during the decomposition of ammonium sulphamate or sulphamic acid (Divers and Haga 1896). The acid so formed decomposes to ammonium hydrogen sulphate which decomposes completely (100% weight loss) in the temperature region 350 to 450° C as seen from the TG and DTA with two endotherms.

3.5. Hydrazinium thiocyanate (N_2H_5SCN)

Hydrazinium thiocyanate is known to rearrange into thiosemicarbazide (Raizman and Thompson 1972). This is similar to the classical rearrangement of ammonium cyanate to urea.



The conversion of hydrazinium thiocyanate to thiosemicarbazide is about 40% when the isomerisation is carried out in solution (Sunner 1957). The conversion of N_2H_5SCN to thiosemicarbazide (74.8%) in solid state was observed has been patented recently (Shirai Kozo *et al* 1976). When N_2H_5SCN was heated isothermally at 100° C for 9 hr at atmospheric pressure, the conversion to thiosemicarbazide was almost 100%. The IR spectrum of the converted sample is superimposable with that of commercial sample (figure 3).

The DTA and TG curves of N_2H_5SCN are shown in figure 4. The TG shows no weight loss upto 125° C. Above this temperature it decomposes with a break at 350° C (weight loss about 70%). On further heating, the decomposition is about 95%. The DTA shows the first endotherm at 98° C due to melting and partial rearrangement of hydrazinium thiocyanate to thiosemicarbazide since the process is dynamic and not enough time is given for complete conversion. Above this temperature there is an equilibrium between these two compounds. The exothermic peak at 156° C is followed by a number of exotherms at 242°, 266°, 310°, 490°, 540°, 590° C, etc., as seen from DTA. The exact nature of these peaks is difficult to assign as TG shows no definite steps corresponding to these temperatures. It is more probable that thiosemicarbazide and hydrazinium thiocyanate react forming a cyclic compound or linear polymeric compound.

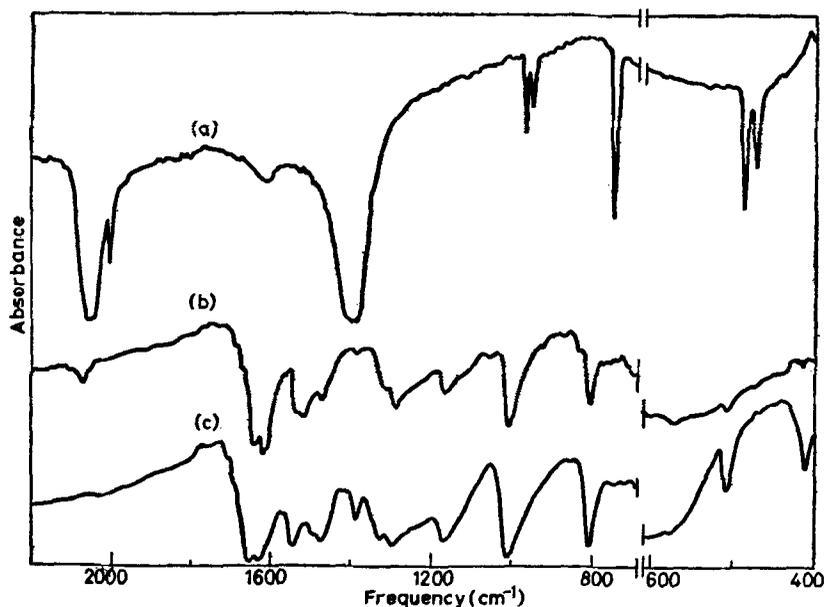


Figure 3. IR absorption spectra of (a) hydrazinium thiocyanate, N_2H_5SCN (KBr pellet); (b) N_2H_5SCN heated at $100^\circ C$ for 9 hr (KBr pellet); (c) thiosemicarbazide standard sample (Nujol mull).

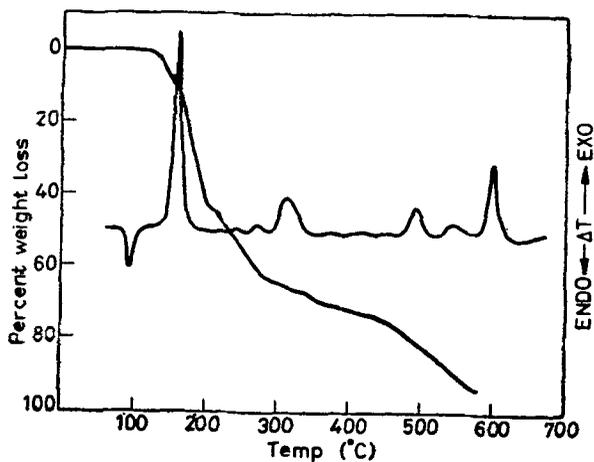


Figure 4. TG and DTA curves of N_2H_5SCN .

4. Conclusions

Hydrazinium metavanadate $N_2H_5VO_3$ has been prepared and reported for the first time. The reactions and thermal properties of $N_2H_5VO_3$ have been studied. The conversion of hydrazinium thiocyanate to thiosemicarbazide is almost quantitative. Thermal properties of hydrazinium acetate, sulphite and sulphamate are also reported for the first time.

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