

Thermal analysis of hydrazinium metal sulphates and their hydrazinates

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Abstract. Thermal analysis of hydrazinium metal sulphates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)$ -I, and their hydrazinates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$ -II, where $M = \text{Fe, Co and Ni}$ have been investigated using thermogravimetry and differential thermal analysis. Type II compounds on heating decompose through an intermediate I and metal sulphate to the respective metal oxides.

Keywords. Thermal analysis ; hydrazinium metal sulphates ; hydrazinates.

1. Introduction

Hydrazinium metal sulphates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$, where $M = \text{Mn, Fe, Co, Ni, Cu, Zn and Cd}$ have been prepared and their spectral and magnetic properties have been reported (Nieuwpoort and Reedijk 1973 ; Cheng *et al* 1977 ; Reiff *et al* 1977 ; Witteveen and Reedijk 1973, 1974 and Klaaijzen *et al* 1975). The interest in these compounds arises from the fact that these compounds exhibit one and three dimensional magnetic interactions of a linear-chain antiferromagnet. Recently, we reported (Patil *et al* 1978, 1979) the preparation of hydrazinates of these hydrazinium metal sulphates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$ ($M = \text{Fe, Co and Ni}$) by the reaction of corresponding metal ammonium double sulphates with hydrazine hydrate. Presently, we report the thermal analysis of both $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ -I and $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$ -II where $M = \text{Fe, Co and Ni}$. For this study we have made use of thermogravimetry (TG) and differential thermal analysis (DTA) techniques. Mössbauer spectra has been used to identify the intermediate in the case of iron compound.

2. Experimental

Hydrazinium metal double sulphates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$, where $M = \text{Fe, Co and Ni}$ were prepared by cocrystallization of hydrazine sulfate with corresponding metal

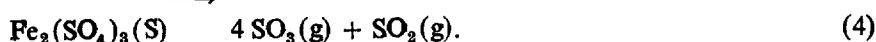
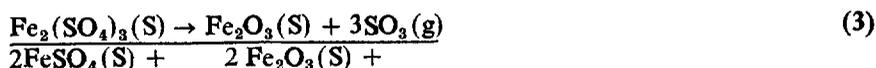
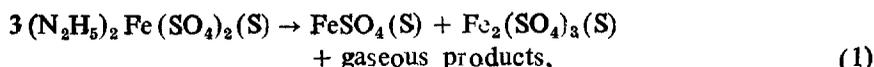
sulphates as described earlier (Nieuwpoort and Reedijk 1973). Hydrazinium metal sulphate hydrazinates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$, where M = Fe, Co and Ni were prepared by the reaction of ammonium metal double sulphate hexahydrates with stoichiometric amounts of hydrazine hydrate as described (Patil et al 1978, 1979). Thermogravimetric analysis (TG) of all the compounds were carried out using stanton Red-Croft thermobalance TG-750. 6-8 mg samples were used for the analysis and the heating rate employed was $10^\circ\text{C min}^{-1}$. Isothermal TG of I was carried out both in nitrogen and in air (figure 1). Differential thermal analysis (DTA) was carried out using manual DTA fabricated in our laboratory which was fitted with Omniscribe strip chart recorder. High temperature DTA was done using DTA 0-2 universal instrument manufactured by Franz Wagner Industrielle Elektronik of German Democratic Republic. Platinum cups were used as sample holder for both TG and DTA. 100 mg samples were used for low temperature DTA and 20 mg for high temperature DTA. Heating rate employed was 7°C min^{-1} . All the experiments were carried out both in air and in nitrogen. The decomposition products of $(\text{N}_2\text{H}_5)_2\text{SO}_4$ were identified by using AEL-MS-10 Mass spectrometer. The gaseous products of $(\text{N}_2\text{H}_5)_2\text{SO}_4$ at 250°C were identified to be NH_3 , H_2O , N_2 and H_2S by $m/e = 17, 18, 28$ and 34 respectively. In addition, $(\text{N}_2\text{H}_5)_2\text{SO}_4$ when heated in a test-tube gave H_2S (characteristic smell) and sulphur (sublimate). Mössbauer spectra of the iron (II and III) compounds were recorded on an EICL MBS 35 spectrometer, operating on multiscalar mode. The values of isomer shift given are with respect to sodium nitroprusside.

3. Results and discussion

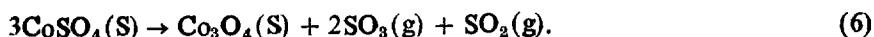
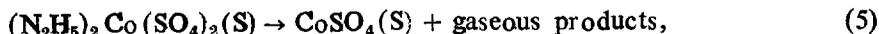
3.1. Thermal decomposition of hydrazinium metal sulphates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$

The TG and DTA data of $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ where M = Fe, Co and Ni are given in table 1 and its isothermal TG curves are given in figure 1. All the double sulphates decompose in two steps. The final product in all the cases is the respective metal oxide. However, the intermediate is different in each case, e.g., in the case of iron salt the intermediate is a mixture of Fe(II) and Fe(III) sulphate, cobalt salt gives cobalt sulphate whereas nickel salt gives a mixture of nickel sulphate and nickel sulphide. The formation of these intermediates has been confirmed by observed weight losses in TG as well as chemical analysis of the TG residues after the first step. In the case of iron salt, the residue obtained at 310°C was gray in colour and hygroscopic. It gave positive test for both Fe(II) and Fe(III) in addition to sulphate. The presence of iron as ferrous was determined quantitatively by volumetric analysis with a standard 0.01 N KMnO_4 ($\% \text{ Fe(II)}$ observed = 14.95; required = 15.18) and the total iron content was determined by EDTA (0.01 M) method after oxidising $\text{Fe(II)} \rightarrow \text{Fe(III)}$ ($\% \text{ Fe}$ observed = 29.89; required = 30.36). The difference gives the amount of Fe(III). The sulphate content was also determined as barium sulphate ($\% \text{ sulphate}$ observed = 68.86; required = 69.64). Further, Mössbauer spectra of the residue of $(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$ decomposed at 310°C shows 3 finger pattern indicating the presence of both Fe^{2+} and Fe^{3+} . The isomer shift, δ , and quadrupole splitting, ΔE_Q , values observed ($\delta = 1.111 \text{ mm/sec}$ and $\Delta E_Q = 2.776 \text{ mm/sec}$

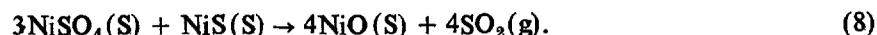
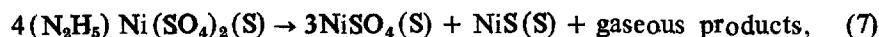
for FeSO_4 and $\delta = 0.339$ mm/sec for $\text{Fe}_2(\text{SO}_4)_3$ are in good agreement with those observed by Duncan and Wigley (1963) and Drago (1971). Similar observations have been made in the case of both $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Bristoti *et al* 1975 and Swamy *et al* 1973) and $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Kohler and Franke 1961 and Frank *et al* 1979) which decompose to give $\text{Fe}_2(\text{SO}_4)_3$. Both FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ on further heating decompose to give Fe_2O_3 . The DTA shows a broad exotherm (310°C) corresponding to the decomposition of $(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$ to a mixture Fe(II) and Fe(III) sulphate followed by an endotherm (702°C) corresponding to the decomposition of iron (II and III) sulphates to Fe_2O_3 . The decomposition steps can be indicated as follows :



The decomposition of $(\text{N}_2\text{H}_5)_3\text{Co}(\text{SO}_4)_2$ is rather simple and the weight loss observed for the first step in TG corresponds to the decomposition of $(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_4)_2$ to cobalt sulphate which on further heating decomposes to give Co_3O_4 . The DTA shows an exotherm (322°C) followed by an endotherm (895°C) corresponding to the TG steps. The decomposition reactions can be represented as follows :



The observed weight loss in the case of hydrazinium nickel sulphate corresponds to the formation of mixture of nickel sulphate and nickel sulphide in the ratio of 3 : 1. Nickel sulphide appears to be formed by the reaction of anhydrous nickel sulphate with $\text{H}_2\text{S}(\text{g})$ or sulphur melt which are the decomposition product of $(\text{N}_2\text{H}_5)_2\text{NiSO}_4$. Formation of nickel sulphide was confirmed by heating the sample in a test-tube and analysing the residue which was partially black. Further, formation of NiS was also seen by passing $\text{H}_2\text{S}(\text{g})$ over anhydrous NiSO_4 around 400°C . The final step corresponds to the decomposition of a mixture of nickel sulphate and nickel sulphide to the NiO. The DTA shows broad exotherm (365°C) followed by an endotherm (853°C) corresponding to the above steps. The decomposition steps can be indicated by equation :



It is interesting to note that the intermediate solid products in the thermal decomposition of $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ are quite different in each case. One can

expect $(N_2H_5)_2M(SO_4)_2$ to decompose with the loss of $(N_2H_5)_2SO_4$ leaving behind the corresponding MSO_4 . However, this trend is seen only in the case of cobalt compound. Isothermal TG both in nitrogen and air (figure 1) of $(N_2H_5)_2M(SO_4)_2$, where $M = Fe, Co$ and Ni show weight loss corresponding to the formation of the above mentioned intermediates. The exact mechanism for the formation of different intermediates appears to be much more complex.

3.2. Thermal decomposition of hydrazinium metal sulphate hydrazinates, $(N_2H_5)_2M(SO_4)_2 \cdot 3N_2H_4$

The TG and DTA data of $(N_2H_5)_2M(SO_4)_2 \cdot 3N_2H_4$ where $M = Fe, Co$ and Ni are tabulated in table 2. All the hydrazinium metal sulphate hydrazinates are fairly stable and decompose to give corresponding hydrazinium metal sulphates (9) which decomposes similar to 3.1, only difference being in the decomposition temperature. Hydrazinium metal sulphates (I) obtained by the dehydrazination of II decompose at a little lower temperature than the chemically prepared salts (I) (tables 1 and 2).

The dehydrazination reaction can be represented as



where $M = Fe, Co$ and Ni .

The double sulphate formation was confirmed by chemical analysis, infra-red spectra and x-ray of the residues obtained after dehydrazination. However, the loss of hydrazine molecules from hydrazinates is different in the case of iron than cobalt and nickel salts. Iron salt shows two step decomposition in TG for the loss of three hydrazine molecules. The first step corresponds to the loss of two hydrazine molecules. This loss of hydrazine is seen as endothermic ($130^\circ C$ and $192^\circ C$) in DTA. The loss of third hydrazine is seen as an exotherm ($254^\circ C$) in DTA. However, in the case of cobalt and nickel TG shows a single step for

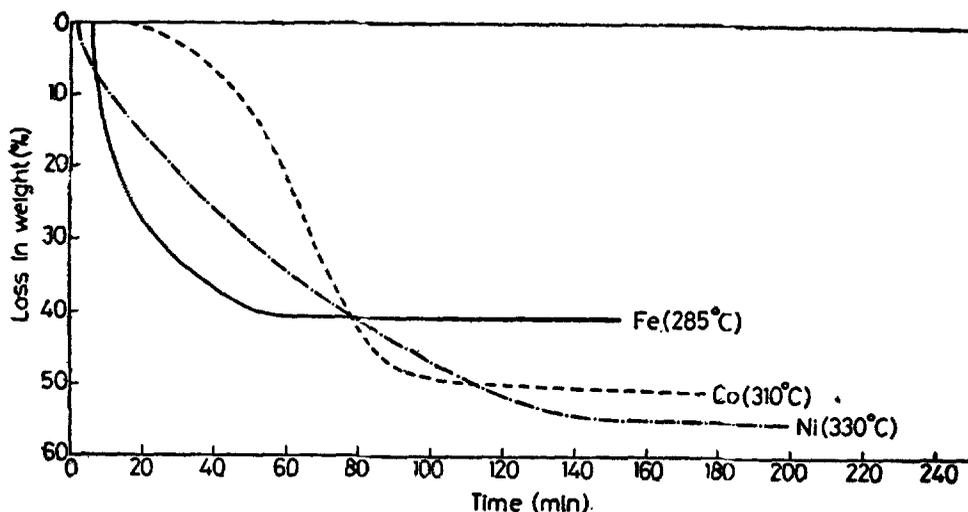


Figure 1. Isothermal TG of $(N_2H_5)_2M(SO_4)_2$ where $M = Fe, Co$ and Ni .

Table 1. Thermal data of $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ where $\text{M} = \text{Fe}, \text{Co}$ and Ni

Compound	Step No.	Thermogravimetry (TG)			DTA peak Temp. ($^{\circ}\text{C}$)	Reactions (Equations)
		Temperature range ($^{\circ}\text{C}$)	Total Weight loss (%)			
			Observed	Required		
$(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$	1	305–392	41.30	41.41	310 (exo)	(1)
	2	671–824	71.80	74.62	702 (endo)	(4)
$(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_4)_2$	1	310–399	50.40	51.12	322 (exo)	(5)
	2	838–970	74.50	74.68	895 (endo)	(6)
$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_4)_2$	1	318–466	56.60	56.15	365 (exo)	(7)
	2	730–927	75.50	76.42	853 (endo)	(8)

Table 2. Thermal data of $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$ where $\text{M} = \text{Fe}, \text{Co}$ and Ni

Compound	Step No.	Thermogravimetry (TG)			DTA peak Temp. ($^{\circ}\text{C}$)	Reactions (Equations)
		Temperature range ($^{\circ}\text{C}$)	Total Weight loss (%)			
			Observed	Required		
$(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	1	35–215	15.40	15.61	130 (endo)	(9)
					192 (endo)	
	2	215–285	23.10	23.42	254 (exo)	(1)
	3	285–350	54.50	55.14	292 (exo)	
$(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	4	637–763	77.10	80.50	688 (endo)	(4)
	1	37–280	23.00	23.24	139 (endo)	(9)
					205 (endo)	
	2	290–419	62.50	62.48	298 (exo)	(5)
$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	3	826–975	79.90	80.57	890 (endo)	(6)
	1	35–269	23.30	23.25	110 (endo)	(9)
				232 (endo)		
$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	2	310–462	66.50	66.39	356 (exo)	(7)
	3	728–941	82.00	81.90	841 (endo)	(8)

the loss of three hydrazine molecule although DTA shows two endotherm and an exotherm similar to iron compound. It is not clear at this stage why the third hydrazine molecule decomposes exothermically.

References

- Bristoti A, Kunrath J I, Viccara P J and Bergter L 1975 *J. Inorg. Nucl. Chem.* **37** 1149
- Cheng C, Wong H and Reiff W M 1977 *Inorg. Chem.* **16** 819
- Drago R S 1971 *Physical methods in inorganic chemistry* (East-West Edition) p. 370
- Duncan J F and Wigley P W R 1963 *J. Chem. Soc.* part I 1120
- Frank E, Varriale M C and Bristoti A 1979 *J. Thermal Anal.* **17** 141
- Klaaijsen, Den Adel H, Dokoupil Z and Huiskamp W J 1975 *Physics B* (Amsterdam) **79** B+C
113
- Kohler K and Franke W 1961 *Fortschr. Mineralog.* **39** 75 ; C.A. 55 21941h
- Nieuwpoort A and Reedijk J 1973 *Inorg. Chim. Acta* **7** 323
- Patil K C, Soundararajan R and Pai Verneker V R 1978 *Proc. Indian Acad. Sci.* **A87** 281
- Patil K C, Soundararajan R and Pai Verneker V R 1979 *Proc. Indian Acad. Sci.* **A88** 211
- Reiff W M, Wong H, Frankel R B and Foner S 1977 *Inorg. Chem.* **16** 1039
- Swamy M S R, Prasad T P and Sant B R 1973 *J. Thermal Anal.* **23** 711
- Witteveen H T and Reedijk J 1973 *Solid State Commun.* **12** 1121
- Witteveen H T and Reedijk J 1974 *J. Solid State Chem.* **10** 151