

THERMAL ANALYSIS OF METAL SULFATE HYDRAZINATES AND HYDRAZINIUM METAL SULFATES

S. GOVINDARAJAN, P.J. BABU and K.C. PATIL

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012 (India)

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ABSTRACT

Thermal analysis of metal sulfate hydrazinates, $\text{MSO}_4 \cdot x\text{N}_2\text{H}_4$ (I) ($\text{M} = \text{Mn, Co, Ni, Zn, Cd}$; $x = 2-3$), hydrazinium metal sulfates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ (II) ($\text{M} = \text{Mn, Cu, Zn, Cd}$), and $\text{N}_2\text{H}_5\text{LiSO}_4$ have been studied using simultaneous TG-DTG-DTA. Both types of complexes, I and II, decompose to the respective metal sulfates or a mixture of metal sulfide and sulfate.

INTRODUCTION

During the course of our studies on hydrazine derivatives, we have reported the preparation, infrared spectra and thermal analysis of a variety of metal hydrazine complexes containing anions like perchlorate, nitrate and azide [1], thiocyanate [2], oxalate [3], formate [4] and hydrazidocarboxylate [5]. We have also studied the preparation, infrared spectra and thermal analysis of some hydrazinium metal sulfates, e.g., $(\text{N}_2\text{H}_5)_2\text{Mg}(\text{SO}_4)_2$ [6], $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ and $(\text{N}_2\text{H}_5)\text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$ ($\text{M} = \text{Fe, Co, Ni}$) [7], $\text{N}_2\text{H}_5\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{N}_2\text{H}_5\text{Al}(\text{SO}_4)_2 \cdot 2\text{N}_2\text{H}_4$ [8]. Recently, the preparation, spectra, thermal analysis and structure of $\text{N}_2\text{H}_5\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm}$) have been investigated [9]. In continuation of these studies, we now report the thermal analysis of $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ ($\text{M} = \text{Mn, Cu, Zn, Cd}$), $\text{N}_2\text{H}_5\text{LiSO}_4$ and some metal sulfate hydrazine complexes, $\text{MSO}_4 \cdot x\text{N}_2\text{H}_4$ ($\text{M} = \text{Mn, Co, Ni, Zn, Cd}$; $x = 2-3$).

EXPERIMENTAL

Metal sulfate hydrazinates, $\text{MSO}_4 \cdot x\text{N}_2\text{H}_4$ (I) ($\text{M} = \text{Mn, Co, Ni, Zn, Cd}$; $x = 2-3$) were prepared by slightly modifying the procedure described in the literature [10-13]. The procedure involved addition of alcoholic hydrazine hydrate to an aqueous saturated solution of metal sulfates. The complexes

TABLE I
Thermoanalytical data of metal sulfate hydrazines

Serial No.	Compound	Percentage of metal		Percentage of hydrazine		Thermogravimetry			DTA peak temp. (°C)	Solid decomposition products	
		Obs.	Calc.	Obs.	Calc.	Step No.	Temp. range (°C)	% weight loss			
				Obs.	Calc.			Obs.	Calc.		
1	$\text{MnSO}_4 \cdot 2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	24.00	23.58	26.70	27.47	1	125-175	7.70	7.73	120 (Endo)	$\text{MnSO}_4 \cdot 2\text{N}_2\text{H}_4$
						2	175-245	21.20	21.46	180 (Exo)	$\text{MnSO}_4 \cdot \text{N}_2\text{H}_4$
						3	245-360	35.00	35.20	300 (Exo)	MnSO_4
2	$\text{CoSO}_4 \cdot 2.75\text{N}_2\text{H}_4$	24.1	24.25	36.30	36.22	1	185-275	26.00	26.35	200 (Exo)	$\text{CoSO}_4 \cdot 0.75\text{N}_2\text{H}_4$
						2	275-385	36.00	36.22	325 (Exo)	CoSO_4
3	$\text{NiSO}_4 \cdot 2.5\text{N}_2\text{H}_4$	24.80	25.00	35.20	34.10	1	230-300	26.00	27.27	280 (Exo)	$\text{NiSO}_4 \cdot 0.5\text{N}_2\text{H}_4$
						2	300-485	41.50	40.91	455 (Exo)	$\text{NiS} \cdot \text{NiSO}_4(1:3)$
4	$\text{ZnSO}_4 \cdot 3\text{N}_2\text{H}_4$	25.90	25.40	37.00	37.30	1	100-165	19.00	18.65	110 (Exo)	$\text{ZnSO}_4 \cdot 1.5\text{N}_2\text{H}_4$
						2	235-310	25.30	24.86	245 (Exo)	$\text{ZnSO}_4 \cdot \text{N}_2\text{H}_4$
						3	310-425	45.00	45.50	350 (Exo)	$\text{ZnS} \cdot \text{ZnSO}_4(1:2)$
5	$\text{CdSO}_4 \cdot 3\text{N}_2\text{H}_4$	37.0	37.0	31.50	31.23	1	155-285	21.00	21.00	175 (Exo)	$\text{CdSO}_4 \cdot \text{N}_2\text{H}_4$
						2	285-385	31.50	31.52	330 (Exo)	CdSO_4

TABLE 2
Thermoanalytical data of hydrazinium metal sulfates

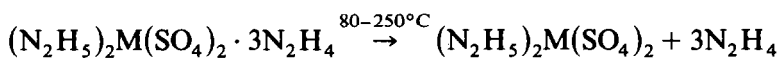
Serial No.	Compound	Chemical analysis (%)				Thermogravimetry				DTA peak temp. (°C)	Solid decomposition products
		Metal		Hydrazine		Step No.	Temp. range (°C)	% weight loss			
		Obs.	Calc.	Obs.	Calc.			Obs.	Calc.		
1	$N_2H_5LiSO_4$	5.90	5.84	23.60	23.53	1	290-345	47.60	47.85	300 (Exo)	$Li_2SO_4 \cdot N_2H_4$
						2	345-435	58.90	59.58	370 (Exo)	Li_2SO_4
2	$(N_2H_5)_2Mn(SO_4)_2$	17.35	17.55	20.20	20.4	1	245-295	40.00	41.53	290 (Exo)	$MnSO_4 \cdot N_2H_4$
						2	295-320	52.00	51.76	305 (Exo)	$MnSO_4$
3	$(N_2H_5)_2Cu(SO_4)_2$	19.55	19.75	19.50	19.90	1	170-300	60.00	60.4	235 (Exo) 245 (Exo)	$CuS + CuSO_4$ (1:1)
4	$(N_2H_5)_2Zn(SO_4)_2$	20.10	20.21	19.70	19.78	1	320-455	57.80	58.92	328 (Exo) 368 (Exo)	$ZnS + ZnSO_4$ (1:1)
5	$(N_2H_5)_2Cd(SO_4)_2$	30.50	30.34	17.30	17.27	1	250-365	44.00	43.74	300 (Exo) 340 (Exo)	$CdSO_4$

precipitated instantaneously and were filtered, washed with alcohol and dried over P_2O_5 in a vacuum desiccator.

Our efforts to prepare copper and iron sulfate hydrazine complexes were not successful. Addition of alcoholic hydrazine to an aqueous solution of copper sulfate resulted in the reduction of Cu^{2+} to metallic copper. On the other hand, $FeSO_4$ solution gave $Fe(OH)_2$. In another method [1], dissolution of iron powder in a solution of $(N_2H_5)_2SO_4$ in $N_2H_4 \cdot H_2O$ gave a solid, presumably $FeSO_4 \cdot xN_2H_4$, which spontaneously ignited during suction filtration. A similar observation was made in the case of $Fe(N_2H_4)_2X_2$ ($X = Cl, Br, I$) [14].

Hydrazinium metal sulfates, $N_2H_5LiSO_4$ and $(N_2H_5)_2M(SO_4)_2$ (II) ($M = Mn, Cu, Zn, Cd$) were prepared by the addition of aqueous solutions of corresponding metal sulfates to a warm solution of $(N_2H_5)_2SO_4$ or $N_2H_6SO_4$. The complexes precipitated instantaneously in all cases except in the case of manganese, which had to be cooled to $10^\circ C$. The products were filtered, washed with distilled water and alcohol, and air dried.

Hydrazinium zinc and cadmium sulfates were also prepared by the dehydrazination of corresponding hydrazinate complexes.



($M = Zn, Cd$). The hydrazinate complexes were obtained by the reaction of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ ($M = Zn, Cd$) with excess hydrazine hydrate as described earlier [7].

The composition of the complexes was fixed by chemical analysis (Tables 1 and 2). The hydrazine content was determined by titration with 0.025 M KIO_3 solution. The metal content was analysed by EDTA titration [7]. Simultaneous TG-DTG-DTA of the complexes were recorded using an ULVAC Sinko-Riku instrument made in Japan. The heating rates employed were 5 and $10^\circ C \text{ min}^{-1}$. Platinum cups were used as sample holders with 6–8-mg samples. All experiments were carried out in air.

Infrared spectra of the complexes were recorded, using a Perkin-Elmer infrared spectrophotometer (781), as nujol mulls.

RESULTS AND DISCUSSION

Metal sulfate hydrazinates

The results of the chemical analysis of the complexes (Table 1) correspond to the formation of metal sulfate hydrazinates of indefinite compositions as previously reported [10–13]. Only manganese forms a hydrated complex and the number of hydrazine molecules in the complexes varies from two to three. Infrared spectra of the complexes show $\nu N-N$ of N_2H_4 in the region

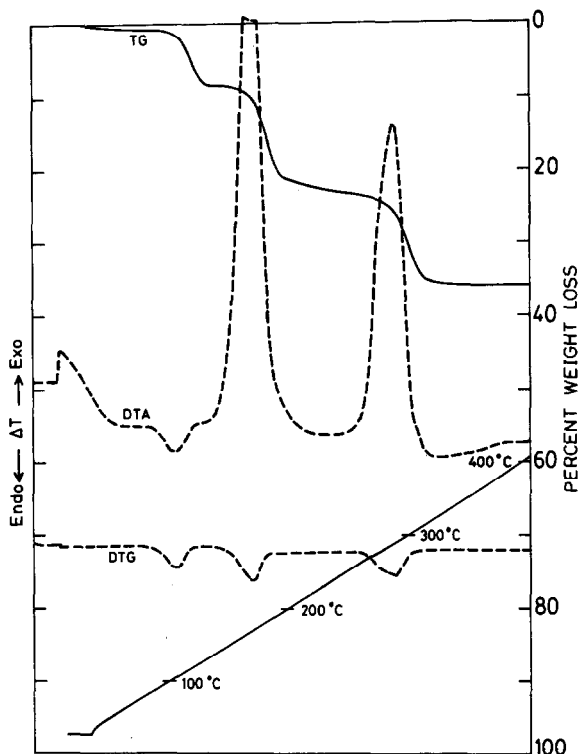


Fig. 1. Simultaneous TG-DTG-DTA of $\text{MnSO}_4(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{O}$.

$960\text{--}980\text{ cm}^{-1}$, indicating the presence of bridged hydrazine [1–5]. The sulfate ion appears to be free (ionic) as seen by the IR absorption bands at $1100\text{ }(\nu_3)$ and $600\text{ cm}^{-1}\text{ }(\nu_4)$ [15]. Coordination of the sulfate groups to the metal ion would result in the lowering of the T_d symmetry of the SO_4 ion and, hence, the splitting of these bands.

The simultaneous TG-DTG-DTA results of the complexes are summarized in Table 1 and a typical thermogram of $\text{MnSO}_4 \cdot 2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ is shown in Fig. 1. It can be seen that all the complexes lose coordinated hydrazine exothermally in more than one step to yield the corresponding metal sulfates. Nickel and zinc complexes gave a mixture of metal sulfide and sulfate.

Hydrazinium metal sulfates

The preparation, structure and infrared spectra of hydrazinium metal sulfates, $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cu}$) have previously been investigated in detail [16–18]. However, thermal analysis of only a few of these complexes has been reported [7,19]. Hydrazinium complexes show infrared absorption around $990\text{--}1005\text{ cm}^{-1}$ characteristic of $\nu\text{N-N}$ of

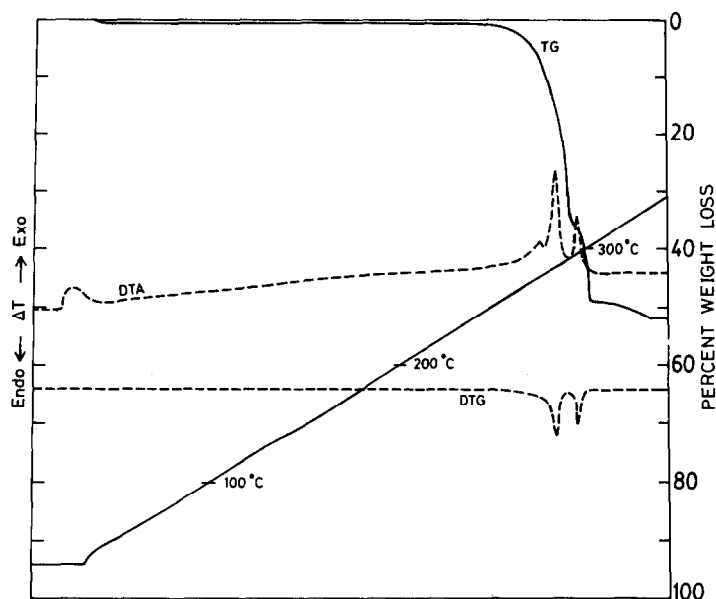


Fig. 2. Simultaneous TG-DTG-DTA of $(\text{N}_2\text{H}_5)_2\text{Mn}(\text{SO}_4)_2$.

the coordinated N_2H_5^+ cation and splitting of ν_3 (1100 cm^{-1}) and ν_4 (600 cm^{-1}) bands of SO_4^{2-} , indicating the presence of bidentate sulfate groups [7,17,18].

The TG-DTG-DTA results of the complexes are summarized in Table 2 and a typical thermogram of $(\text{N}_2\text{H}_5)_2\text{Mn}(\text{SO}_4)_2$ is shown in Fig. 2. Hydrazinium lithium sulfate decomposes exothermally to yield lithium sulfate through lithium sulfate hydrazinate. This behaviour is similar to the decomposition of $(\text{N}_2\text{H}_5)_2\text{Mg}(\text{SO}_4)_2$ which also decomposes to MgSO_4 through an $\text{MgSO}_4 \cdot \text{N}_2\text{H}_4$ intermediate [6].

Transition metal complexes decompose exothermally to give the corresponding metal sulfate or a mixture of metal sulfide and sulfates. Manganese and cadmium complexes gave corresponding metal sulfates as end products. Both copper and zinc complexes decomposed to give a mixture of metal sulfide and sulfates similar to iron, cobalt and nickel complexes [7]. It is interesting to note that whereas the TG-DTG of the complexes show single-step decomposition, DTA exhibits two exotherms in all cases. A possible explanation for this discrepancy could be the dynamic nature of TG compared to DTA. The probable intermediate in the decomposition of $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ complexes may be the corresponding $\text{MSO}_4 \cdot \text{N}_2\text{H}_4$ which, being unstable at the temperature at which it is formed, decomposes to yield the corresponding metal sulfate as end product. Further proof for this comes from the decomposition temperatures of metal sulfate hydrazinates (Table 1) which are comparable to those of the second exotherm (Table 2) for the respective metal complexes.

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