Thermochimica Acta, 71 (1983) 53–57
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL REACTIVITY OF METAL FORMATE HYDRAZINATES

P RAVINDRANATHAN and K C. PATIL

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

(Received 6 June 1983)

ABSTRACT

Metal formate hydrazinates, $M(HCOO)_2(N_2H_4)_2$, where M = Mn, Co, Ni, Zn or Cd, have been prepared and characterized by chemical analysis and infrared spectra. The thermal decomposition of the complexes has been studied using thermogravimetry and differential thermal analysis. With the exception of nickel, all the metal formate hydrazinates initially lose hydrazine endothermically and the dehydrazinated metal formates decompose exothermically in air to give the corresponding metal oxides.

INTRODUCTION

During the course of our studies on hydrazine derivatives, we have reported the preparation and thermal properties of hydrazinium metal sulfate hydrazinates [1,2], metal hydrazine nitrate, perchlorate and azide complexes [3], and metal oxalate hydrazinates [4]. In continuation of this study, it was thought interesting to study the thermal decomposition of metal formate hydrazinates. Although the preparation of metal formate hydrazinates has been reported [5], there appears to be no information on their thermal analyses. In this paper, we report the results of thermal analysis of a few metal formate hydrazinates, $M(HCOO)_2(N_2H_4)_2$, where M = Mn, Co, Ni, Zn or Cd.

EXPERIMENTAL

Metal formate hydrazinates were prepared by the addition of excess hydrazine hydrate (99–100%) to the corresponding metal formate hydrates. The reaction was instantaneous with the evolution of heat.

$$M(HCOO)_2 \cdot (H_2O)_2 + 2\,N_2H_4 \cdot H_2O \rightarrow M(HCOO)_2(N_2H_4)_2 + 4\,H_2O \quad (1)$$

where M = Mn, Co, Ni, Zn or Cd. The products were filtered and washed with alcohol and ether and dried over phosphorus pentoxide. The composi-

0040-6031/83/$03 00

tions of the complexes were determined by chemical analysis and characterized by infrared spectra. The hydrazine content in all the complexes was determined by titrating against 0.025 M KIO_3 under Andrews' conditions [6]. The metal content was determined volumetrically using a standard EDTA solution [6].

The infrared spectra of the samples were recorded as nujol mulls and KBr discs using a Perkin-Elmer 599 spectrophotometer.

Thermogravimetry (TG) and differential thermal analysis (DTA) experiments were carried out using a Stanton-Redcroft thermobalance TG 750 and a DTA instrument fabricated in our laboratory [7], respectively. Both the TG and DTA were carried out in air and the heating rate employed was 10°C min^{-1}. Platinum cups were used as sample holders. 6–8 mg samples were used for TG and 50–100 mg for DTA.

Electron spin resonance (ESR) spectra of the samples were obtained using a Varian E 109 ESR spectrometer.

X-Ray diffraction patterns of the residues were obtained with a Philips PW 1050/70 diffractometer using CuK_α and CoK_α radiation.

The magnetic susceptibility of the complexes was measured using a Gouy balance at room temperature. Mercury tetrathiocyanato cobaltate, $[HgCo(CNS)_4]$, was used as calibrant.

RESULTS AND DISCUSSION

Chemical analysis of the samples (Table 1) conforms with the assigned composition of $M(HCOO)_2(N_2H_4)_2$ where M = Mn, Co, Ni, Zn or Cd. The corresponding Fe and Cu analogues could not be prepared for the reasons given. The iron formate hydrazinate was highly unstable and decomposed as soon as it was isolated. In the case of the copper complex, addition of hydrazine hydrate to cupric formate hydrate resulted in the reduction of the latter to metallic copper.

The infrared spectra of the complexes (Table 2) show the characteristic

TABLE 1

Chemical analysis data of $M(HCOO)_2(N_2H_4)_2$

M	Metal		Hydrazine	
	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)
Mn	26.38	26.20	29.30	30.63
Co	27.87	27.66	29.17	30.08
Ni	27.41	27.58	29.39	30.11
Zn	29.84	29.70	30.57	29.15
Cd	41.82	42.19	23.93	24.02

TABLE 2

Infrared absorption frequencies of $M(HCOO)_2(N_2H_4)_2$(cm^{-1})

Mn	Co	Ni	Zn	Cd	Assignment
3320	3340	3350	3340	3340	N–H stretching
3290	3310	3320	3320	3310	
3250	3270	3200		3260	
3140				3180	
2715	2820	2820	2750	2820	C–H stretching
	2750	2700	2740	2720	
1620	1640	1650	1645	1620	NH_2 bending
1570	1605	1615	1620	1600	COO asymmetric stretching
		1580			
1380	1405	1410	1410	1410	C–H bending
1290	1340	1350	1380	1380	COO symmetric stretching
		1230	1340	1340	
1190	1185	1190	1185	1160	NH_2 wagging
1180		1170			
970	980	985	980	980	N–N stretching
790	780	775	780	760	OCO bending
775	750	760	745		
	710	745			
615	650	685	650	650	NH_2 asymmetric rocking
525	580	625	580	550	NH_2 symmetric rocking
328	382	410	318	335	M–N stretching
325					

ν_{N-N} absorption (980 cm^{-1}) of bridged hydrazine [8]. The IR absorption frequencies of the formate ion (C_{2v} symmetry) have been reported [9]. The important characteristic frequencies of the formate ion in transition metal formates and rare earth formates have also been studied [10]. Since the hydrazine is bridged to the metal, the formate group appears to be unidentate. If the metal is directly attached to one of the oxygen atoms in the formate group, then the frequency corresponding to $-C{=}O$ (1700 cm^{-1}) should have been observed [11]. The absence of this band clearly shows that the M–O bond is not purely covalent. Apart from these facts, the observed OCO asymmetric and symmetric stretching vibrations are at 1605 and 1380 cm^{-1}, respectively, and, consequently, it is concluded that the M–O bonds must be essentially electrostatic [9,12]. Similar observations have been made with regard to acetate complexes [9]. Room temperature magnetic susceptibility values of the Co (5.1220 BM) and Ni (3.2751 BM) complexes suggest that in these complexes hydrazine could act as a bridging bidentate ligand and formate as a unidentate ligand.

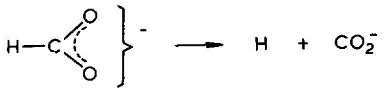
The thermal decomposition of metal formates has been studied by several authors [13–16]. Metal formates are known to decompose exothermically in

TABLE 3

Thermal analysis data of $M(HCOO)_2(N_2H_4)_2$

M	Step no.	Thermogravimetry			DTA peak temp (°C)	Products
		Temp range (°C)	Total wt. loss			
			Found (%)	Calcd (%)		
Mn	1	110–178	17 00	15.31	170(endo) 192(endo)	$Mn(HCOO)_2N_2H_4$
	2	197–320	72.00	62.20	272(exo)	MnO, Mn_2O_3
Co	1	100–204	28.00	30.05	161(endo)	$Co(HCOO)_2$
	2	204–447	62.50	63 50	200(exo) 224(exo) 280(exo)	Co_3O_4
Ni	1	116–233	68.00	64.87	217(exo)	Ni, NiO
Zn	1	110–324	29.00	29.17	168(endo)	$Zn(HCOO)_2$
	2	324–512	61.00	62.90	449(exo)	ZnO
Cd	1	100–284	25.00	24.02	187(endo)	$Cd(HCOO)_2$
	2	284–598	52.00	51 80	289(exo) 362(exo) 407(exo)	CdO

a single step to the respective metal oxides or the metal, depending upon the conditions [10,13,17]. However, alkali and alkaline earth metal formates are reported [18] to decompose through oxalate intermediates. Oxalate intermediates have also been proposed for the decomposition of La, Eu and Sc formates [19,20]. Formation of oxalates has been explained by the CO_2 radical reaction. The results of TG and DTA studies of $M(HCOO)_2(N_2H_4)_2$ are summarized in Table 3. With the exception of nickel, all the other complexes decompose in two steps. In the case of manganese, the weight loss observed for the first step corresponds to the loss of one hydrazine molecule, whereas in cobalt the weight loss corresponds to the loss of two hydrazine molecules, and then the second step takes place to form MnO, Mn_2O_3 and Co_3O_4. The nickel complex decomposes in a single step to give a mixture of nickel oxide and nickel metal [10]. Zinc and cadmium complexes decompose in two steps. They yield coloured intermediates as the product of the first step in the decomposition. ESR spectra of these intermediates show the presence of radicals with *g* values of 1.972. The IR spectrum of these intermediates is similar to that of the metal formates. It has been reported [18] that, when irradiated, alkali metal formates decompose photochemically to yield CO_2^- radicals which can be written as



(2)

This CO_2^- was detected by ESR studies and it can be argued that reaction

(2) could be possible here. These coloured intermediates of Zn and Cd undergo further exothermic decomposition yielding the corresponding oxides.

It is reasonable to assume that such radical intermediates are formed even in the case of Mn, Co and Ni complexes but could not be isolated as they appear to be more reactive. The structures of the final products were confirmed by X-ray powder diffraction.

Unlike metal oxalate hydrazinates, metal formate hydrazinates do not exhibit autocatalytic decomposition/combustion behaviour. This may be due to the loss of hydrazine (endothermically) at lower temperatures before the exothermic decomposition of the metal formates. For autocatalysis, the decomposition of hydrazine and metal salt should occur simultaneously [4].

ACKNOWLEDGEMENT

One of us (P.R.) wishes to thank Dr. J.P. Vittal for assistance in obtaining TG measurements.

REFERENCES

1 K C. Patil, S Govindarajan, R. Soundararajan and V R. Pai Verneker, Proc Indian Acad. Sci. Sect. A, 90 (1981) 421.
2 S Govindarajan and K.C Patil, Thermochim. Acta, 55 (1982) 373
3 K.C Patil, C. Nesamani and V R. Pai Verneker, Synth. React Inorg. Met.-Org. Chem., 12 (1982) 383.
4 K.C Patil, D. Gajapathy and K. Kishore, Thermochim. Acta, 52 (1982) 113.
5 F J Arnaiz Garcia, An. Quim., 73 (1977) 1121, Chem Abstr., 89 (1978) 206719n.
6 A.I Vogel, Textbook of Quantitative Inorganic Analysis, Longmans, London, 3rd edn., 1961, p. 380
7 K Kishore, V.R. Pai Verneker and M.R. Sunitha, J. Appl. Chem. Biotechnol, 27 (1977) 415
8 A.I Braibanti, F. Dallavalle, H.A. Pellinghelli and E. Leporti, Inorg Chem., 7 (1968) 1430
9 K. Itoh and H.J Bernstein, Can J. Chem., 34 (1956) 170.
10 G. Rama Rao, K.C Patil and C.N.R Rao, Inorg. Chim. Acta, 4 (1970) 215.
11 K Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978
12 K.B. Harvey, B.A. Morrow and H.F. Shurvell, Can. J Chem, 41 (1963) 1181.
13 D. Dollimore and K.H. Tonge, J Inorg. Nucl. Chem., 29 (1967) 621
14 D. Dollimore, J P Gupta and D V. Nowell, Thermochim Acta, 30 (1979) 339
15 Le Van My, Bull Soc Chim. Fr, (1965) 366.
16 V Zepletal, J. Jedlicka and V. Ruzika, Chem Listy, 50 (1956) 1406
17 S Shishido and Y Masuda, Nippon Kagaku Zasshi, 94 (1973) 185.
18 G D. Buttress and M.A Hughes, J. Chem. Soc. A, (1968) 1272
19 S R. Dharwadkar, M.S. Kumbhar, M.S. Chandrasekhariah and M D Karakanawala, J. Inorg. Nucl Chem., 42 (1980) 1621
20 M. Shyamala, S R. Dharwadkar and M S. Chandrasekhariah, Thermochim. Acta, 56 (1982) 135.