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THERMAL REACTIVITY OF METAL OXALATE HYDRAZINATES

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ABSTRACT

Metal oxalate hydrazinates $MC_2O_4\ 2\ N_2H_4$ where M = Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd have been prepared and characterised by chemical analysis and infrared spectra Thermal reactivity and decomposition of these oxalato complexes have been studied using thermogravimetry and differential thermal analysis Hydrazinates of Mn, Fe, Co, Ni and Cu oxalates exhibit autocatalytic decomposition behaviour whereas the others do not This phenomenon can be attributed to the presence of a bridged hydrazine as well as the thermal stability of the anhydrous metal oxalates

INTRODUCTION

Recently we reported the preparation of metal hydrazido carbonates $M(N_2H_3COO)_2$—I [1] where M = Mn, Co, Ni, Cu and Zn and metal hydrazido carbonate hydrazinates $M(N_2H_3COO)_2(N_2H_4)_2$—II [2,3] where M = Fe, Co and Ni. Thermal analysis of these compounds [1,3] showed some interesting features. For example both I and II decompose exothermically in air. Complexes of type I decompose through the corresponding metal oxalate and carbonate intermediates to the respective metal oxides.

$$M(N_2H_3COO)_2 \rightarrow MC_2O_4 + 2\ NH_3 + N_2 \tag{1}$$

$$MC_2O_4 \rightarrow MCO_3 + CO \tag{2}$$

$$2\ MCO_3 \xrightarrow{O_2} M_2O_3 + 2\ CO_2 \tag{3}$$

On the other hand complexes of type II decompose through a reactive intermediate (x) (which could not be isolated) to the respective oxides. Further, type II compounds exhibit autocatalytic decomposition whereas type I compounds do not show such behaviour. This difference in reactivity between I and II could be attributed to the presence of hydrazine in II. Because of the similarity of I and II one can speculate the possible intermediate (x) during the thermal decomposition of II to be an oxalato compound. The possible reaction sequence could be written as

$$M(N_2H_3COO)_2(N_2H_4)_2 \rightarrow \underset{(x)}{MC_2O_4(N_2H_4)_2} + 2\ NH_3 + N_2 \tag{4}$$

$$2\,MC_2O_4(N_2H_4)_2 \xrightarrow{O_2} M_2O_3 + 2\,NH_3 + N_2 + 4\,CO_2 + H_2O \qquad (5)$$

The observed reactivity of the intermediate (x) could then be understood since metal oxalates decompose exothermically in air and combustion is expected to be autocatalytic because of the presence of hydrazine fuel.

A survey of the literature revealed that a number of metal oxalate hydrazinates have been prepared and their thermal properties studied by Krylov and co-workers [4–8]. However their studies do not indicate the observed reactivity.

In order to test our hypothesis we have now prepared a number of metal oxalate hydrazinates $MC_2O_4(N_2H_4)_2$ where M = Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd by different methods and characterised them by conventional chemical analysis and infrared spectra. Thermal reactivity of these hydrazinates has been investigated by thermogravimetry (TG) and differential thermal analysis (DTA)

EXPERIMENTAL

Metal oxalate hydrazinates $MC_2O_4(N_2H_4)_2$ where M = Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd were prepared by any of or all the methods described below.

I Reaction of metal oxalate hydrates with hydrazine hydrate

Freshly prepared metal oxalate hydrates were treated with stoichiometric quantities of 99–100% hydrazine hydrate. The mixture was thoroughly stirred for a few minutes. The reaction was instantaneous with evolution of heat. Change in colour of the original salt was also observed in the case of few salt, e.g.

Iron	bright yellow	→	light yellow
Cobalt	light pink	→	dark pink
Nickel	light green	→	blue

$$MC_2O_4\cdot 2\,H_2O + 2\,N_2H_4\cdot H_2O \rightarrow MC_2O_4\cdot 2\,N_2H_4 + 4\,H_2O \qquad (6)$$

The products were analysed chemically and found to be $MC_2O_4(N_2H_4)_2$ where M = Mn, Fe, Co, Ni, Zn and Cd.

II Reaction of metal powder with ammonium oxalate in hydrazine hydrate

When metal powder (eg. Mg, Fe, Co, Zn, Cu etc.) is added to a solution of ammonium oxalate in hydrazine hydrate it dissolves with the evolution of heat, hydrogen and ammonia. The product on chemical analysis was found to be $MC_2O_4(N_2H_4)_2$.

$$M + (NH_4)_2C_2O_4\cdot H_2O + 2\,N_2H_4\cdot H_2O \rightarrow MC_2O_4(N_2H_4)_2 + 3\,H_2O + H_2 + 2\,NH_3 \qquad (7)$$

where M = Mg, Fe, Co, Zn, Cu.

In the case of copper the product $CuC_2O_4 \cdot 2\ N_2H_4$ is highly unstable, loses a molecule of hydrazine in air and forms the monohydrazinate as the stable product.

III Reaction of aqueous solutions of metal salts with ammonium oxalate in hydrazine hydrate

When an aqueous solution of metal salt was mixed with ammonium oxalate in hydrazine hydrate, corresponding metal oxalate hydrazinates were precipitated.

$$M^{2+} + (NH_4)_2C_2O_4 \cdot H_2O + 2\ N_2H_4 \cdot H_2O \rightarrow MC_2O_4(N_2H_4)_2 + 3\ H_2O + 2\ NH_4^+ \qquad (8)$$

where M = Fe, Co and Ni.

Hydrazine content in all these compounds was determined by volumetric analysis using standard 0.025 M KIO_3 solution under Andrews' conditions [9]. Oxalate content was determined either volumetrically using standard $KMnO_4$ solution or gravimetrically precipitating as calcium oxalate monohydrate. Metal content was determined by volumetric analysis using standard EDTA solution.

Infrared spectra were recorded as nujol mulls using a Perkin Elmer 599 spectrophotometer.

Thermogravimetry (TG) was carried out using a Stanton-Redcroft thermobalance TG750. Heating rate employed was 10°C per minute. 6–8 mg of each sample were used in a platinum cup. All experiments were carried out in air.

Differential thermal analysis (DTA) was done up to 500°C using an instrument described elsewhere [10] fitted with an omniscribe strip chart recorder. The heating rate employed was 10°C per minute. 50 mg of each sample were used in a platinum sample holder. All experiments were done in air.

RESULTS AND DISCUSSION

The results of the chemical analysis (Table 1) show that there is a good agreement between observed and calculated values of metal, oxalate and hydrazine contents for the proposed formula $MC_2O_4(N_2H_4)_2$ where M = Mg, Mn, Fe, Co, Ni, Zn and Cd and $CuC_2O_4 \cdot N_2H_4$. The infrared spectral data of these complexes have been tabulated in Table 2 and the assignments are made on the basis of earlier studies [11–14]. In all these complexes the metal has octahedral coordination. The main feature of the infrared results is that hydrazine is present as a bridged ligand as is seen by the fact that the $\nu_{N\text{-}N}$ of $N_2H_4 \sim 960\ cm^{-1}$ [14] and the $C_2O_4^{2-}$ is bonded to the metal as a bidentate [11,13].

Thermal analysis data of the compounds have been summarised in Table 3. The composition of the intermediates and products are fixed by the observed weight loss in TG, as well as by chemical analysis, IR and X-ray powder pattern. Thermogravimetric results are in agreement with the DTA data.

TABLE 1

Analytical data

Compound	Hydrazine	Metal	Oxalate
	Found (Calc)	Found (Calc)	Found (Calc)
$MgC_2O_4 \cdot 2\,N_2H_4$	35.4 (36.2)	14.4 (13.8)	49.8 (50.0)
$MnC_2O_4 \cdot 2\,N_2H_4$	31.3 (30.8)	25.9 (26.5)	41.6 (42.5)
$FeC_2O_4 \cdot 2\,N_2H_4$	30.4 (30.8)	27.2 (26.8)	40.8 (42.4)
$CoC_2O_4 \cdot 2\,N_2H_4$	30.3 (30.3)	27.0 (28.0)	42.0 (41.7)
$NiC_2O_4 \cdot 2\,N_2H_4$	30.6 (30.3)	27.0 (27.9)	41.3 (41.8)
$CuC_2O_4 \cdot N_2H_4$	17.2 (17.4)	33.4 (34.6)	48.3 (47.9)
$ZnC_2O_4 \cdot 2\,N_2H_4$	28.6 (29.4)	31.0 (30.1)	39.9 (40.5)
$CdC_2O_4 \cdot 2\,N_2H_4$	24.2 (24.2)	42.3 (42.5)	32.1 (33.3)

The salient features of the thermal analysis are:

a) all oxalate hydrazinate complexes decompose exothermically

b) manganese and iron complexes decompose in a single step and show autocatalytic decomposition

c) the cobalt complex decomposes in two steps and exhibits autocatalytic decomposition

d) copper and nickel complexes decompose in three steps.

The copper complex loses one molecule of hydrazine at room temperature itself. Both of them exhibit autocatalytic decomposition

e) Mg, Zn and Cd complexes decompose in more than two steps and do not show autocatalytic behaviour.

The observed difference in the decomposition pattern and reactivity could be explained on the basis of the thermal stability of the anhydrous metal oxalates and the nature of the $M-N_2H_4$ bonding in these complexes. Since the decomposition temperatures of MnC_2O_4 ($T_d = 275°C$) and FeC_2O_4 ($T_d = 235°C$) [15] coincide with the temperature at which N_2H_4 is lost from $M(N_2H_4)_2^{2+}$ complexes we see single step decompositions, as in the case of Mn and Fe complexes. However in the case of other transition metal oxalate hydrazinates as we go from Co ($T_d = 260°C$), Ni ($T_d = 350°C$) to Cu ($T_d = 310°C$) the decomposition temperature of MC_2O_4 varies from 260–350°C. Therefore we see that the hydrazine molecules are lost successively without the decomposition of the metal oxalates. Infrared results also confirm this observation. It can be seen that ν_{M-N} in these complexes changes from 340 cm^{-1} in Mn, Fe, Co etc. to 400 cm^{-1} in the case of nickel and 460 cm^{-1} in the case of copper, indicating weak $M-N_2H_4$ bonding in the case of Ni and Cu complexes, respectively.

The decomposition of Zn, Cd and Mg complexes appears to follow an entirely different path. Unlike other transition metal ions, Zn and Cd have a completed *d* shell and the decomposition of $ZnC_2O_4(N_2H_4)_2$ and $CdC_2O_4(N_2H_2)_2$ appears to be similar to $MgC_2O_4(N_2H_4)_2$. Both Mg and Zn complexes decompose to give a yellow

TABLE 2

Infrared spectral data of MC_2O_4 2 N_2H_4 where M=Mg, Mn, Fe, Co, Ni, Zn, Cd and CuC_2O_4 N_2H_4

Mg	Mn	Fe	Co	Ni	Cu	Zn	Cd	Assignment
	3330 (s)	3300 (s)	3300 (s)	3320 (s)	3480 (s)	3300 (s)	3310 (s)	N–H · O stretching (H-bonded)
3200 (b)	3250 (s)	3220 (s)	3240 (s)	3240 (b)	3200 (b)	3260 (s)	3250 (s)	N–H asym stretching
	3180 (s)	3120 (s)	3150 (s)	3160 (s)		3200 (s)	3160 (s)	N–H sym stretching
				3090 (b)				
1610 (b)	1695 (b)	1660 (s)	1665 (s)	1635 (s)	1660 (b)	1660 (b)	1650 (b)	C–O asym. stretching
	1625 (b)	1640 (s)	1620 (w)		1600 (b)	1620 (w)	1600 (b)	
		1620 (w)						
		1600 (s)						
		1580 (s)	1585 (s)	1560 (m)		1590 (m)		NH_2 deformation
1320 (vs)	1310 (vs)	1305 (s)	1300 (s)	1320 (s)	1370 (m)	1320 (s)	1310 (vs)	C–O sym stretching + O–C=O bending
1280 (vs)		1290 (vs)		1295 (s)	1345 (w)	1300 (s)		
					1300 (s)			
					1280 (s)			
1100 (s)	1135 (vs)	1190 (s)	1200 (s)	1215 (s)	1230 (s)	1200 (s)	1175 (vs)	NH_2 twisting and wagging
		1160 (s)	1180 (s)	1180 (m)	1200 (s)	1120 (s)	1120 (s)	
		1120 (s)		1150 (m)				
955 (m)	965 (vs)	980 (w)	960 (m)	980 (m)	990 (s)	960 (vs)	960 (vs)	N–N stretching
915 (m)		960 (s)						
820 (s)	785 (vs)	775 (vs)	780 (vs)	780 (vs)	795 (s)	780 (vs)	775 (vs)	O–C–O bending
		760 (s)			765 (s)	755 (vs)	760 (vs)	
600 (s)	640 (vs)	625 (s)	625 (w)	640 (s)	665 (s)	620 (w)	650 (b)	M–O stretching + C–C stretching
		595 (s)		600 (s)				
495 (w)	540 (s)	495 (w)	550 (b)	500 (w)	500 (s)	530 (m)	550 (s)	O–C–O bending + C–C–O bending
	505 (s)	465 (w)		460 (w)		500 (m)	510 (m)	
360 (s)	375 (m)	365 (s)	365 (m)	400 (s)	450 (s)	340 (b)	340 (b)	M–N stretching
	340 (vs)	340 (m)	340 (w)					

TABLE 3

Thermal data

Sample No	Compound	Step no	Thermogravimetry Temp range (°C)	Weight loss Found	Weight loss Calc	DTA peak temp (°C)	Reaction
1	$MnC_2O_4\ 2N_2H_4$	1	204–225	60.9	61.9	217 (exo)	$2\,MnC_2O_4(N_2H_4)_2 \rightarrow Mn_2O_3$
2	$FeC_2O_4\ 2N_2H_4$	1	180–310	60.2	61.6	202 (exo)	$2\,FeC_2O_4(N_2H_4)_2 \rightarrow Fe_2O_3$
3	$CoC_2O_4\ 2N_2H_4$	1	204–258	16.1	15.2	209 (exo)	$CoC_2O_4(N_2H_4)_2 \rightarrow CoC_2O_4\ N_2H_4$
		2	258–358	60.4	61.2	262 (exo)	$3\,CoC_2O_4(N_2H_4)_2 \rightarrow Co_3O_4$
4	$NiC_2O_4\ 2N_2H_4$	1	226–258	14	15.2	219 (exo)	$NiC_2O_4(N_2H_4)_2 \rightarrow NiC_2O_4\ N_2H_4$
		2	258–331	32	30.4	244 (exo)	$NiC_2O_4(N_2H_4)_2 \rightarrow NiC_2O_4$
		3	331–419	63	64.6	290 (exo)	$NiC_2O_4(N_2H_4)_2 \rightarrow NiO$
5	$CuC_2O_4 \cdot N_2H_4$	1	152–181	17	17.4	148 (exo)	$CuC_2O_4 \cdot N_2H_4 \rightarrow CuC_2O_4$
			181–370	58	56.6	274 (exo)	$CuC_2O_4\ N_2H_4 \rightarrow CuO$
6	$ZnC_2O_4\ 2N_2H_4$	1	120–215	16	14.7	216 (exo)	$ZnC_2O_4(N_2H_4)_2 \rightarrow ZnC_2O_4\ N_2H_4$
		2	215–350	30	29.4	301 (exo)	$ZnC_2O_4(N_2H_4)_2 \rightarrow ZnCO_2;\ NH_2 \cdot N_2$
		3	350–466	64	62.6	406 (exo)	$ZnC_2O_4(N_2H_4)_2 \rightarrow ZnO$
7	$CdC_2O_4\ 2N_2H_4$	1	169–181	11	12.1	182 (exo) 291 (exo)	$CdC_2O_4\ (N_2H_4)_2 \rightarrow CdC_2O_4 \cdot N_2H_4$
		2	248–456	51	51.4	353 (exo)	$CdC_2O_4 \cdot (N_2H_4)_2 \rightarrow CdO$
8	$MgC_2O_4\ 2N_2H_4$	1	35–215	19	18.2	205 (exo)	$MgC_2O_4\ 2N_2H_4 \rightarrow MgC_2O_4\ N_2H_4$
		2	215–484	34	36.1	407 (exo)	$MgC_2O_4\ 2N_2H_4 \rightarrow MgCO_2\ NH_2\ N_2$
		3	484–688	78	77.1	530 (exo)	$MgC_2O_4\ 2N_2H_4 \rightarrow MgO$

coloured intermediate which has been identified as $MCO_2^- \cdot NH_2(N_2)$ where M = Mg or Zn by TG wt. loss, ESR and IR spectra. The presence of the CO_2 radical in this intermediate is evidenced by an ESR signal with $g = 2.0034$. It is known that MgC_2O_4 decomposes via the formation of such a radical [16]. Infrared spectra of these intermediates shows strong absorption at ~ 2200 cm^{-1} corresponding to $\nu_{N \equiv N}$ as in dinitrogen complexes [17]. Further details of this nitrogen complex will be published elsewhere.

It is interesting to note that transition metal oxalate hydrazinates $MC_2O_4(N_2H_4)_2$, where M = Mn, Fe, Co, Ni and Cu, when touched with a glowing splinter ignite and exhibit autocombustion yielding the corresponding metal oxides. The observed autocombustion behaviour of Mn and Fe complexes is as expected since they decompose in a single step. However Co, Ni and Cu complexes which decompose in more than one step also exhibit autocombustion. This behaviour could be attributed to the higher heating rates during combustion compared with decomposition as well as the larger sample sizes used for combustion. The exothermicity of the decomposition of the hydrazine is enough to ignite the metal oxalates e.g. in the case of $FeC_2O_4(N_2H_4)_2$, when a strand of the sample is ignited in air the maximum temperature of the condensed phase has been recorded as 560°C using a chromel–Alumel thermocouple although the ignition temperature is 180°C. Further, a close examination of the TG curves and thermal analysis data reveals that the decomposition is continuous with short breaks. Thus, one can now understand why the intermediate (x) during the decomposition of $M(N_2H_3COO)_2(N_2H_4)_2$–II where M = Fe, Co and Ni could not be isolated. $MC_2O_4 \cdot (N_2H_4)_2$ formed by the thermal decomposition of II appears to be very reactive and caught fire when exposed to air. Another factor responsible for the autocatalytic behaviour might be the catalytic activity of the transition metal oxides formed. It has been established that transition metal oxides, e.g. Fe_2O_3, catalyse the decomposition of hydrazine [18].

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