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THERMAL BEVAVIOUR OF THE COORDINATION COMPOUND $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$

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Abstract

Thermoanalytical, mass spectrometric and X-ray diffraction data were associated with a reliable assignation of the thermal transformations of the coordination compound $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$.

Keywords: $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$, thermochemistry

Introduction

The literature mentioned thermal behaviour studies of some coordination compounds containing urea as ligand, respectively $[Cu(urea)_4]Cl_2$ [1] and $[Al(urea)_6](NO_3)_3$ [2].

This paper, the first from a larger series dedicated to a systematic study of the thermal behaviour of two classes of coordination compounds characterized by molecular formula $[M(urea)_6]L_2 \cdot nH_2O$ and $[MFe_2(urea)_6]L_8 \cdot nH_2O$ where M=Co^{2+}, Mn^{2+}, Ni^{2+} and L=NO_3^-, CH_3COO^-, reports the thermochemical behaviour of the coordination compound $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$.

Experimental

The coordination compound with molecular formula $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ (confirmed by elemental analysis) is obtained by a solid state method. Details about the synthesis method and physico-chemical characterization are presented elsewhere [3]. X-ray diffraction patterns were obtained by using a Philips difractometer with a CuK_α radiation. Thermochemical investigations were carried out on a NETZSCH STA 409 coupled to a BALZERS QMS 421 mass spectrometer, under dynamic air and nitrogen flow (20 $cm^3\ min^{-1}$), with samples mass about 20 mg at heating rate of 2 $K\ min^{-1}$.

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Results and discussion

The TG, DTG and DTA curves are depicted in Figs 1–2. The most representative ion intensities curves are selected in Figs 3–6. Table 1 summarizes the thermogravimetric data.

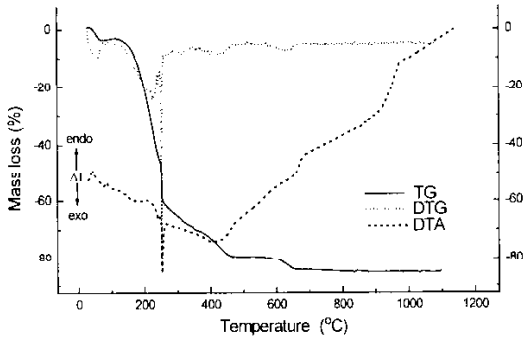

Fig. 1 Thermoanalytical curves of $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ (nitrogen)

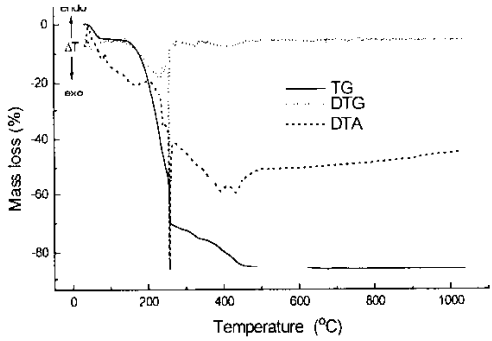

Fig. 2 Thermoanalytical curves of $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ (air)

In the temperature range 30–1200°C the decomposition of urea compound occurs in seven/eight stages of weight loss. The experimental total weight loss recorded from the TG curves is 86.25/86.94% (nitrogen/air) in comparison with the theoretical one of 86.64%, calculated considering the solid residue as Mn_3O_4. Although the similar profiles of the obtained thermoanalytical curves, differences between the two experiments arose from the third decomposition step.

The thermal decomposition of the investigated coordination compound is a complex one, due do the multidirectional course of decomposition/transformation of urea and the presence in coordination coumpound of both reducing and oxidizing agents (urea and nitrate ions).

The thermal decomposition of the coordination compound begins by the evolving of two hygroscopic or hydration water molecules. The dehydration reaction is followed by the melting of the anhydrous compound at 83.5°C.

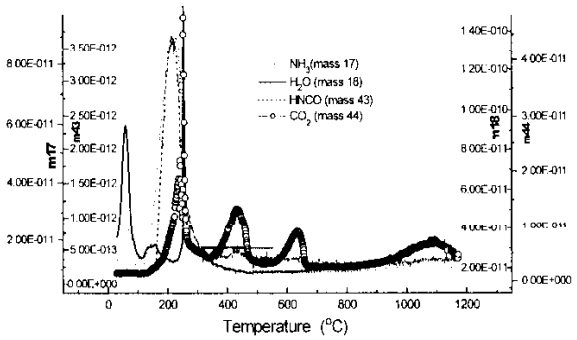

Fig. 3 Ion intensities curves of $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ (nitrogen)

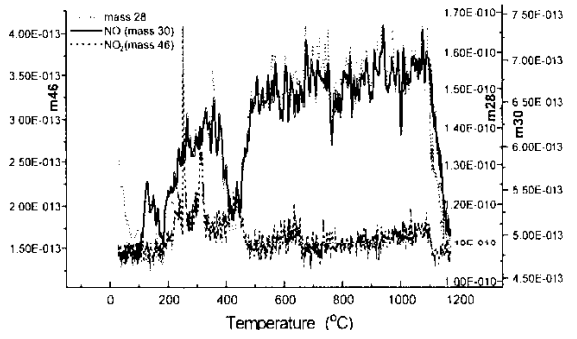

Fig. 4 Ion intensities curves of $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ (nitrogen)

The next region of weight loss corresponding to the release of four urea molecules, is rather complicated, being an overlapping of at least three decomposition steps. The splitting of the DTG curves and the different temperatures of the maximum amounts of the evolved products justify this affirmation. The reaction starts with an endothermic decomposition of urea in ammonia and cyanic acid [4]:

$$NH_2\text{–}CO\text{–}NH_2 \rightarrow [OCN]NH_4 \rightarrow HNCO + NH_3 \qquad (1)$$

The intermediate $[OCN]NH_4$ was discerned only under nitrogen atmosphere. Such a reaction progress determines the appearance of two peaks in the mass spectrum, corresponding to $[NH_4]$ and $[OCN]^+$. A similar decomposition mechanism was mentioned for urea's thermal transformation [5]. Due to a partial evolving of the anion NO_3^-, above 150/135°C (nitrogen/air) the reaction changes to an exothermic one.

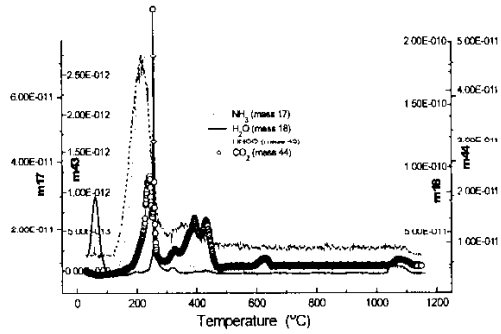

Fig. 5 Ion intensities curves of $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ (air)

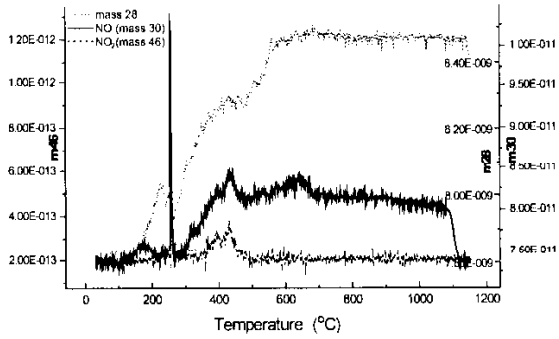

Fig. 6 Ion intensities curves of $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ (air)

Among the decomposition products NH_3, HNCO, CO_2 are identified and traces of NO_2. In air atmosphere a small amount of ammonia is oxidized to NO and water is formed.

The presence of CO_2 was clearly identified by MS method, due to the comparable shape of the curves corresponding to m/z= 44 $[CO_2]^+$ and m/z=12 $[C]^+$. In principle, N_2O (m/z= 44 too) can be also formed at the expense of NO. In this case, however oxygen should also be formed and it was not observed.

In accordance with reaction's (1) stoichiometry, the detected amount of HNCO and NH_3 should be compared. Actually, the amount of HNCO is smaller in comparison with the NH_3 one. One can advance two main reasons: firstly, its reaction with undecomposed urea yielding compounds of biuret and triuret type:

$$H_2NCONH_2 + HNCO \rightarrow H_2NCONHCONH_2 \quad (2)$$

$$H_2NCONHCONH_2 + HNCO \rightarrow H_2NCONHCONHCONH_2 \quad (3)$$

Table 1 Thermoanalytical data of the compound $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$

Decomposition step	$T_i - T_f$/ °C*	$T_{max\,(DTG)}$/ °C	$T_{max\,(DTA)}$/ °C	Mass loss/ %	Thermal effect	Assignation
nitrogen	38.2–77.8	54.7	42.1	5.39	endo	release of two hygroscopic or hydration water molecules
			83.5		endo	melting
2	122.9–247.1	150.9	141.9	42.57	exo	release of four molecules of urea
3	247.1–284.1	252.8	252.8	17.41	exo	release of NO_3^-, release of two molecules of urea, oxidation of ammonia and oxidation Mn^{2+} to Mn^{4+}
4	284.1–336.9			4.3	exo	final oxidation of ammonia
5	336.9–469.2	434.7	408.3	10.38	exo	decomposition of biuret, triuret type compound
6	569.1–667.9	635	653.9	4.85	exo	conversion of MnO_2 to Mn_2O_3
7	984.1–1151.1			1.1	exo	conversion of Mn_2O_3 to Mn_3O_4

Table 1 Continued

Decomposition step	T_i–T_f/ °C*	$T_{max(DTG)}$/ °C	$T_{max(DTA)}$/ °C	Mass loss/ %	Thermal effect	Assignation
air	37.2–82.8	56.1	41.2	5.11	endo	release of two hygroscopic or hydration water molecules
1			83.5		endo	melting
2	126.8–252.5	140.2	170.9	39.85	exo	release of four molecules of urea
3	252.5–272.1	256.8	256.8	26.63	exo	release of NO_3^-, release of two molecules of urea, oxidation of ammonia and oxidation Mn^{2+} to Mn^{4+}
4	272.1–343.8	320.8		4.41	exo	final oxidation of ammonia
5	343.8–412.2	391.8	392.8	5.34	exo	decomposition of biuret, triuret type compound
6	412.2–460.1	422.1	433.1	4	exo	
7	586.9–657.8	633.8		1.03	exo	conversion of MnO_2 to Mn_2O_3
8	972–1141.2			0.75	exo	conversion of Mn_2O_3 to Mn_3O_4

*T_i, T_f: initial and final temperature of transformation

Secondly, its great instability in the conditions of the MS analysis, due to the cleavage into the fragments m/z=14 and m/z=29 ($[N]^+$ and $[HCO^+]$) [6].

The third decomposition step in which the whole amount of nitrate ion is released, is a strong, fast oxidation process. It is characterized by the maxima of the DTG, DTA, H_2O, CO_2, NO_2 curves at 252.8/256.8°C (nitrogen/air). In addition, under air flow maximum amount of NO is detected also at 256.8°C. Under air flow experiment the decomposition reaction is more energeting, determining a nearly double weight loss and the oxidation of the whole amount of nitrogen present in reaction medium. The reaction mechanism can be considered a self-initiated one. It is initiated by the evolving of nitrate ion which oxidizes both ammonia (producing water and nitrogen oxides) and Mn^{2+} to Mn^{4+} (yielding MnO_2). MnO_2 propagates the reaction, working as an in situ oxidant of the biuret and triuret compounds formed earlier.

A final oxidation of ammonia with generation of NO_2 occurs in the fourth decomposition step. Under air flow HNCO and CO_2 are found also among the evolved products. The main phases discerned in the solid intermediates after this decomposition step are MnO_2 and Mn_2O_3. The conversion $MnO_2 \rightarrow Mn_2O_3$ is emphasized in the intermediate obtained under air flow, due to a higher participation of MnO_2 to the reactions with carbonaceous materials.

The next three/four decomposition stages associated with weak exothermic effects are assigned to the decomposition of biuret and triuret type compounds. As reaction products for these last oxidation reactions were identified:

– in the range 330–460°C under nitrogen flow NO_2, a single decomposition step, CO_2 and HNCO. Under air flow, two decomposition steps, CO_2 , and nitrogen compounds HNCO, N_2, NO and NO_2 are evolved.

– in the range 570–670°C, NO, N_2, CO_2 , traces of $[NH]^{2+}$, HNCO, and NO_2.

– in the range 970–1150°C, H_2O and CO_2. Traces of NO were also detected.

If the temperature range of thermal decomposition occurrence for the first/two reactions of this decomposition region are close as urea's decomposition [2], the last two decomposition steps are strictly related with the temperatures of manganese oxides transformations [7]:

$$6MnO_2 \xrightarrow[-\frac{1}{2}O_2]{580\text{–}620^\circ C} 3Mn_2O_3 \xrightarrow[\frac{1}{2}O_2]{950\text{–}1110^\circ C} 2Mn_3O_4$$

evolution confirmed by the phase analysis of the intermediates and end products.

In conclusion, by means of thermoanalytical and mass spectrometric measurements, the following thermal decomposition stoichiometry of the $[Mn(urea)_6](NO_3)_2 \cdot 2H_2O$ compound may be assumed:

$$[Mn(urea)_6](NO_3)_2 \cdot 2H_2O \rightarrow [Mn(urea)_6](NO_3)_2 \rightarrow [Mn(urea)_2](NO_3)_2 \rightarrow$$
$$\text{mixture of } (Mn_2O_3 \cdot MnO_2) + \text{carbonaceous residia} \rightarrow$$
$$Mn_2O_3 + \text{carbonaceous residia} \rightarrow Mn_3O_4$$

where the carbonaceous residia consist in biuret in triuret type compounds.

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