Thermochimica Acta, 224 (1993) 217–225
Elsevier Science Publishers B.V., Amsterdam

Thermal properties of neodymium hydrazidocarbonate trihydrate

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(Received 8 January 1993; accepted 2 February 1993)

Abstract

The thermal properties of lanthanide hydrazidocarbonates were studied in an inert atmosphere by selecting neodymium hydrazidocarbonate trihydrate, $Nd(N_2H_3COO)_3 \cdot 3H_2O$, as a model substance for the essentially similar thermal behaviour of hydrazidocarbonates of all the lanthanides except promethium. Neodymium hydrazidocarbonate trihydrate cannot be converted into a pure anhydrous compound by heat treatment because the dehydration of the sample is accompanied by partial decomposition of the other part of the molecule, i.e. the hydrazidocarbonato groups. The decomposition finally proceeds through some intermediates to a mixture of neodymium oxide and amorphous carbon, and finally at 1450°C, to neodymium oxide carbide, $Nd_2C_2O_2$.

INTRODUCTION

Hydrazine as a basic reagent readily absorbs carbon dioxide and transforms first into hydrazinium hydrazidocarbonate and, following prolonged introduction of this gas, into hydrazidocarbonic acid N_2H_3COOH [1]. The reactions between aqueous solutions of this reagent and various metal cations yield complex products. In these compounds, the hydrazidocarbonato group acts as a bi- or tridentate ligand and coordinates the central cations through one or both oxygen atoms forming five-membered rings [2]. Most research so far has been directed to the study of the syntheses, structures and thermal properties of these products and to the determination of some of their IR characteristics [3–6]. Hydrazidocarbonates have been prepared with some transition elements and some main group elements. The lanthanide group of elements presented the possibility of synthesizing new hydrazidocarbonates and of comparing them with already isolated products. We have synthesized the hydrazidocarbonates of all the lanthanides except promethium [7].

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The thermal properties of this set of compounds have been studied in an inert argon atmosphere. Owing to the similarity of the lanthanides, a detailed study of the thermal behaviour of neodymium hydrazidocarbonate trihydrate as a representative of the whole group has been made.

EXPERIMENTAL

The synthesis of $Nd(H_2H_3COO)_3 \cdot 3H_2O$ was carried out according to the literature [4] by the reaction of a solution of neodymium trichloride and a solution of diluted hydrazine hydrate saturated by carbon dioxide, by prolonged bubbling of this gas through a solution of hydrazine hydrate.

The compositions of the initial compound, the intermediates and the final products were determined by chemical analysis. The hydrazine content of the samples was determined by potentiometric titration with potassium iodate (V) [8]. Neodymium was determined by indirect complexometric titration in the presence of arzenazo-1 indicator at pH 6 [9] and carbon dioxide, gravimetrically, acidimetrically or by ion-selective electrode [10, 11]. The total nitrogen content in the samples was determined by Kjeldahl's method, and the cyanide and cyanate by the corresponding standard methods.

The thermal properties were determined in argon on Mettler TA1 and Netzsch STA 409 instruments in the range from ambient temperature to 1600°C. The gases evolved during the thermal analysis were determined by Varian 1420 gas chromatograph and an Inficon Leybold Heraeus Quadrex 200 quadropole mass spectrometer connected on-line to the thermobalance. IR spectra were taken on a Perkin-Elmer 521 spectrometer. X-ray powder diffraction data were obtained by a Guinier de Wolff camera with Cu $K\alpha$ radiation. For the identification of the products, the CD-ROM data base PDF2 set 1-39 was used.

The composition of the starting compound, $Nd(N_2H_3COO)_3 \cdot 3H_2O$, conformed with the formula Nd, 34.06% calc., 34.1% obt.; N_2H_4, 22.70%, calc., 22.7% obt.; CO_2, 31.18% calc., 30.0% obt. The difference of 13.9% was attributed to water (calc. 12.76%).

RESULTS AND DISCUSSION

The thermal properties of neodymium hydrazidocarbonate trihydrate $Nd(N_2H_3COO)_3 \cdot 3H_2O$ were studied in an argon atmosphere. The inert atmosphere was chosen to determine the thermal stability and the course of the thermal degradation of the sample without the oxidizing effects that occur in air. The hydrazidocarbonato group is sensitive to oxidation because it is a derivative of hydrazine, a very strong, endothermic compound also used as a rocket propellant [12].

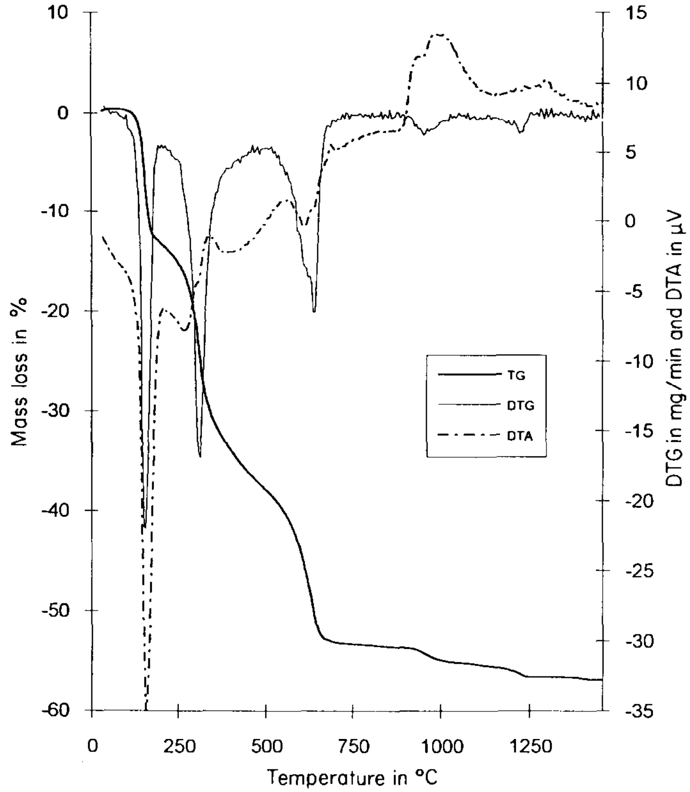

Fig. 1. Thermoanalytical curves for $Nd(N_2H_3COO)_3 \cdot 3H_2O$.

A general overview of the thermal properties was made on a 100 mg sample. The curves for the thermal decomposition of the sample are given in Fig. 1. The decomposition proceeds in seven major steps.

The decomposition is very complex due to the constitution of the sample and to the diversity of possible reactions and recombinations of the components that can occur during the thermal treatment of the sample. To have a better insight into the reactions taking place in the furnace, intermediates were isolated. The temperatures at which the intermediates were isolated differ somewhat from the temperatures obtained in the experiment for characterization of the thermal properties of neodymium hydrazidocarbonate trihydrate as given in Fig. 1. To prepare ample amounts of intermediates for the chemical and other characterization methods, sample weights of 1000 mg were used which caused some shifting of the peak temperatures and temperature intervals at which the intermediates were isolated. Figure 2 gives the TG curves and temperature profiles for the evolved gas as obtained by EGA.

The largest difference between the 100 and 1000 mg sample weights is observed in the first step of the thermal decomposition. The initial temperature for the 1000 mg sample is 85°C followed by a DTG peak at

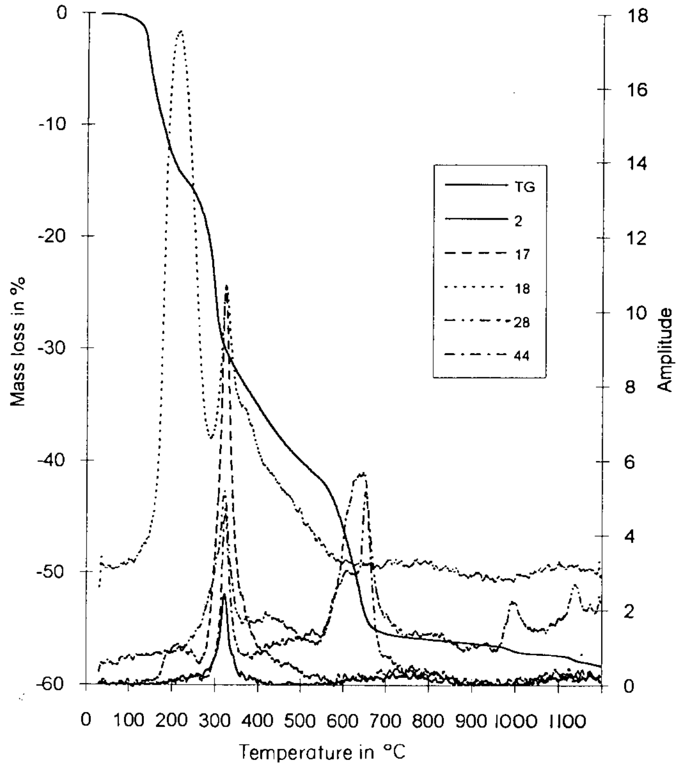

Fig. 2. EGA curves for $Nd(N_2H_3COO)_3 \cdot 3H_2O$, where numbers in inset correspond to *m/z* values obtained by quadrupole mass spectrometry: 2, H_2; 17, NH_3; 18, H_2O; 28, N_2 and/or CO; 44, CO_2.

152°C. The mass loss up to 228°C is 14.8%. The dehydration of the sample takes place in this temperature interval but pure anhydrous neodymium hydrazidocarbonate cannot be prepared in large amounts in this way because some breaking up of the hydrazidocarbonato rings accompanies the dehydration. This is evident from the actual mass loss of 14.8% compared to the calculated mass loss for the dehydration of 12.76%, but in the case of the ten-fold smaller sample weight, the calculated mass loss is almost obtained, i.e. 12.8%. The evolved gas analysis on the larger sample reveals that the release of water is also accompanied by evolution of some ammonia and nitrogen. The chemical analysis of the intermediates and final product is given in Table 1.

The dehydration of the sample progresses into the second decomposition step with a DTG peak at 295°C. The rate of mass loss diminishes appreciably at 340°C and an intermediate was isolated at this temperature. Mass loss up to this temperature is 31.4%.

The decomposition in this interval is complex and intensive transformations and recombinations of the constituents take place as confirmed by the analysis of the evolved gases. Ammonia, nitrogen, hydrogen, carbon

TABLE 1

Chemical analyses (%) of the starting compound $Nd(N_2H_3COO)_3 \cdot 3H_2O$ and the intermediates

Temperature/ °C	N_2H_4	Nd	CO_2	H_2O
20	22.7	34.1	30.0	13.9
228	24.4	39.8	34.6	–
340	5.1	49.8	20.8	–
470	0.4	57.7	13.6	–
730	–	76.8	–	–
1000	–	76.5	–	–
1190	–	84.5	–	–

dioxide and water were detected. The molar ratio N_2H_4:Nd:CO_2 in the intermediate is 0.46:1:1.46. Ammonia, nitrogen and carbon dioxide are the decomposition products of the hydrazidocarbonato group. Although the dehydration of the sample was completed in the first step, water is again found in the evolved gases. The presence of water is due to the reaction of the hydrogen or hydrogen-containing constituents with the CO_2 in the N_2H_3COO group. Although all the above-mentioned data are available, it is still hard to determine the composition of the intermediate.

The temperature interval from 340 to 470°C corresponds to the next step of the thermal degradation. The mass loss at 470°C is 38.7% but the TG curve does not level off at this temperature. The chemical analysis of the intermediate reveals that practically all the hydrazine (except 0.4%) has decomposed or left the sample. Carbon dioxide can still be determined in the residue giving a molar ratio of Nd:CO_2 = 1:0.77.

Heating the sample from 470 to 730°C, with a DTG peak at 639°C, represents the next, more distinctive step of the thermal decomposition. Mass loss up to this temperature is 55.5%. Neither hydrazine nor carbon dioxide are present in the residue. The neodymium content is 76.8% which is close to the value calculated on the basis of the mass loss and its initial concentration, e.g. 77.45%. Although hydrazine is not present in the intermediate, the determination of the total nitrogen revealed a content of 11.3% giving a molar ratio Nd:N = 1:1.5. No cyanide was detected in the residue. The exact nature of the nitrogen bonding in the residue is not known.

The IR spectra of the residue obtained in the previous step revealed a strong band at 2180 cm^{-1} and a band of the same intensity at 2060 cm^{-1} which could correspond to a variety of components such as NCO, CNO, CN_2, CO [13]. The presence of the cyanide was excluded by the chemical analysis but nitrogen could also be present as cyanate or cyanamide, or in some other form. The presence of the cyanamide is very probable and is

TABLE 2

Powder diffraction data of the intermediates

730°C		1000°C		1190°C		1450°C	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
9.40	10	8.30	8	3.30	8	7.10	6
5.20	9	4.15	8	2.990	8	3.55	8
4.15	10	3.34	8	2.890	10	3.41	8
3.80	8	3.10	10	2.210	8	3.37	6
3.65	8	2.750	8	1.905	8	3.20	2
3.35	8	2.600	8	1.700	8	3.10	10
3.10	10	2.130	8	1.605	7	2.970	9
2.750	8	1.930	9	1.590	6	2.890	3
2.600	6	1.880	4	1.445	2	2.600	6
2.560	7	1.750	7	1.270	3	2.380	7
2.180	5	1.675	2	1.220	3	2.360	7
2.130	7	1.640	7			1.980	7
1.960	3	1.580	8			1.960	8
1.930	9	1.550	2			1.930	7
1.880	3	1.480	2			1.860	3
1.840	3	1.430	2			1.785	1
1.750	3	1.300	1			1.700	2
1.670	1	1.250	2			1.680	1
1.640	1	1.210	1			1.660	2
1.580	5					1.620	1
						1.600	1
						1.580	1
						1.550	1
						1.505	1
						1.420	1

further supported by the fact that in the case of the thermal analysis of a similar compound, zinc hydrazidocarbonate, the presence of zinc cyanamide was confirmed by X-ray diffraction in the residue obtained at 730°C [14]. Actually, 4.6% of cyanate was determined in the sample but this could also be due to hydrolysis of the cyanamide during the preparation and analysis of the sample. The presence of carbonyl may be the result of the relatively high temperatures employed.

The evaluation of the X-ray powder diffraction data given in Table 2 and a search of the CD-ROM database PDF2 set 1-39 did not reveal any similarities of the obtained diffraction patterns with the published data.

In the next step of the thermal decomposition, starting at 730°C with a DTG peak at 989°C and ending at 1000°C, the mass loss is 1.4%, giving a cumulative mass loss of 56.9% up to this temperature. The neodymium content in the residue is 76.5%. No other components were determined in this intermediate, but the black colour of the sample implied the presence of carbon. The composition nature of the sample was confirmed by dissolving the residue in hydrochloric acid. Part of the sample remained undissolved. The filtered and dried black residue burned in oxygen to carbon dioxide, as confirmed by gas chromatography. The ratio between neodymium and carbon residue determine gravimetrically was 1:0.49. This carbon originates from the decomposition of the last neodymium intermediate. The IR spectrum of the residue reveals strong bands at 2065 and 645 cm^{-1}, a medium band at 720 cm^{-1} and weak bands at 3300, 3215 and 1160 cm^{-1}.

Heating the sample to 1190°C yields a DTG peak at 1131°C and the release of additional amounts of carbon. Its content in the residue determined as above was 6.7%, giving a ratio Nd:C = 1:0.95. The weight loss from 1000°C up to this temperature is 1·2%. The analysis of the evolved gases revealed only the presence of nitrogen. Contrary to the analysis of the last two intermediates, the diffraction patterns revealed the presence of Nd_2O_3 in the high-temperature A form [15]. No IR bands in the region around 2000 cm^{-1} were observed (1150 w, 960 w, 720 m and 530 w).

Heating the sample to the final temperature of 1450°C produced a cumulative mass loss of 59.5%. The end product of the thermal decomposition as determined by X-ray powder diffraction is neodymium oxide carbide $Nd_2O_2C_2$ [16], accompanied by a lesser amount of the above-mentioned high-temperature form of Nd_2O_3. The neodymium content of 83.7% closely coresponds to the calculated content for $Nd_2O_2C_2$, i.e. 83.74%. The analysis of the evolved gases revealed only the presence of nitrogen in the furnace carrier gas.

The suggested course of the thermal decomposition of $Nd(N_2H_3COO)_3 \cdot 3H_2O$ in inert argon atmosphere is given in Table 3.

CONCLUSIONS

The thermal decomposition of the hydrazidocarbonate trihydrates of the lanthanides series (except promethium) in an argon atmosphere is very complex due to their components. The very reactive hydrazidocarbonato group, which is a derivative of hydrazine, decomposes and a variety of decomposition schemes, transformations and intermediates is possible. The processes occurring during the heat treatment were analysed for neodymium hydrazidocarbonate trihydrate which was chosen as a model substance for all thirteen lanthanide compounds. The decomposition follows several steps. At the beginning of the decomposition the decomposition/transformation of the hydrazine is faster than that of the COO part of the hydrazidocarbonato group. The thermal degradation of the sample proceeds at 730°C with formation of an intermediate with a substantial amount of cyanamide. It is complete at 1450°C, with the end

TABLE 3

Suggested course of the thermal decomposition of $Nd(N_2H_3COO)_3 \cdot 3H_2O$ in inert argon atmosphere

Step	Temperature/°C	Reaction	Evolved gases
1	228	Dehydration of the starting compound to $Nd(N_2H_3COO)_3$	$H_2O \gg NH_3$, N_2
2	340	Decomposition of hydrazido-carbonato groups and interactions of the constituents	H_2O, NH_3, H_2, N_2, CO_2
3	470	Decomposition of hydrazido-carbonato groups and	H_2O, NH_3, H_2, N_2, CO_2
4	730	Formation of the cyanamide intermediate	N_2, CO_2
5	1000	Decomposition of the cyanamide and formation of amorphous carbon	N_2
6	1190	Further decomposition of the cyanamide, formation of amorphous carbon and Nd_2O_3	N_2
7	1450	Formation of $Nd_2C_2O_2$	

product being neodymium oxide carbide formed from the neodymium oxide and amorphous carbon both obtained at 1190°C.

ACKNOWLEDGEMENTS

The authors express their gratitude to the late Professor Dr. Jože Slivnik for initiating this work, to Borka Sedej for chemical analyses and Barbara Novosel M.Sc. for the EGA measurements.

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