

STUDIES OF THERMAL DECOMPOSITION OF HYDRAZIDOCARBONATES OF SOME FIRST ROW TRANSITION ELEMENTS*

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The thermal properties of some hydrazidocarbonates of copper, $\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$, nickel, $\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{N}_2\text{H}_4$, and iron, $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$ and $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$, were studied in an inert argon atmosphere. The TG, DTG and DSC curves for these compounds were taken. In the case of $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$, intermediates were observed and isolated during the decomposition. The end-products were metal powders oxidized to a greater or lesser degree.

Due to their occurrence, abundance and economic importance, carbonates of various elements have frequently been the object of study by thermoanalytical methods in order to determine their properties, their behaviour during thermal treatment, and the products which may arise in this way. Besides these "genuine" carbonates, a number of derivatives of carbonic acid are known, one of them being hydrazidocarbonic acid with its related compounds, the hydrazidocarbonates. Hydrazidocarbonic acid can be thought of as derived from carbonic acid by substitution of one hydroxy group by a hydrazido group (N_2H_3^-).

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The properties of these compounds justify their designation as hydrazidocarbonates. The acid can be prepared by bubbling carbon dioxide through an aqueous solution of hydrazine overnight [1]:



Aqueous solutions of hydrazidocarbonic acid react with solutions of various metal salts to give hydrazidocarbonates as products [2-11].

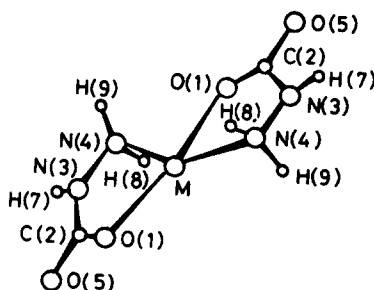


Fig. 1 Five membered rings of hydrazido-carbonates

The X-ray structural determination of these compounds reveals that the hydrazidocarbonato group can act as a bi- or tridentate ligand (Fig. 1), forming five-membered rings and coordinating the central cation through O(1) and N(4) for a bi-, and also through O(5) for a tridentate arrangement [12-17]. Water, hydrazine or hydrazinium(1+) ions can also be found in various types of hydrazidocarbonates (Table 1).

Table 1 Diverse types of hydrazido-carbonates

Types	<i>n</i>	<i>m</i>
$\text{M}(n)(\text{N}_2\text{H}_3\text{COO})_n$	1, 2, 3	
$\text{M}(n)(\text{N}_2\text{H}_3\text{COO})_n \cdot m\text{H}_2\text{O}$	1, 2, 3	0.5, 1, 2, 3
$\text{M}(n)(\text{N}_2\text{H}_3\text{COO})_n \cdot \text{H}_2\text{O} \cdot \text{N}_2\text{H}_4$	2	
$\text{M}(n)(\text{N}_2\text{H}_3\text{COO})_n \cdot m\text{N}_2\text{H}_4$	2	1, 2
$\text{K}[\text{M}(n)(\text{N}_2\text{H}_3\text{COO})_{n+1}]$	2	
$\text{N}_2\text{H}_5[\text{M}(n)(\text{N}_2\text{H}_3\text{COO})_{n+1}] \cdot m\text{H}_2\text{O}$	2, 3	1, 3

The thermal properties of these compounds differ markedly from the those of "conventional" carbonates, mainly due to the thermal and reducing properties of the hydrazido group and its decomposition products [18-20].

Experimental

The starting materials were prepared according to literature methods.

Copper(II) hydrazidocarbonate semihydrate, $\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$, was prepared from a dilute aqueous solution of hydrazine hydrate saturated with carbon dioxide and a solution of copper(II) chloride [9]. The precipitate, which forms at once, was filtered off, washed and dried.

Iron(II) hydrazidocarbonate, $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$, was prepared by reaction of an aqueous solution of hydrazine hydrate saturated with carbon dioxide and a solution of iron(II) chloride. The molar ratio of iron to hydrazine was 1:5 [8].

Nickel(II) hydrazidocarbonate dihydrazine was prepared in the same way as the analogous cobalt compound [19], by solvolysis of finely pulverized hydrazinium(1+) tris-hydrazidocarbonatonickelate(II) monohydrate, $\text{N}_2\text{H}_5[\text{Ni}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$.

Hydrazinium(1+) tris-hydrazidocarbonatoferrate(II) monohydrate, $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$, was prepared by reaction of an aqueous hydrazine hydrate solution saturated with carbon dioxide and iron(II) chloride. The molar ratio of iron to hydrazine was 1:16 [9]. Chemical analyses of the starting compounds are reported in Table 2.

Table 2 Chemical analysis of the starting compounds

Compound	Mc.	Mf.	N ₂ H _{4c.}	N ₂ H _{4t.}	CO _{2c.}	CO _{2t.}
$\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$	28.55	28.0	28.75	28.0	39.54	-
$\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$	27.13	26.5	30.09	30.6	42.75	41.7
$\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{N}_2\text{H}_4$	21.52	21.6	46.94	46.2	32.27	-
$\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$	16.83	16.1	38.57	38.9	39.78	40.5

The thermal properties (TG, DTG, DSC and EGA) of the compounds in question were investigated on a Mettler TA3000 System. The experimental conditions were: sample weights 10-50 mg, heating rate 4 or 10 deg/min, crucibles $\alpha\text{-Al}_2\text{O}_3$ with a volume of 140 μl , carrier gas flow rate 20 l/h. The decomposition reactions of the hydrazidocarbonates were also examined by thermal decomposition of larger samples (1 g) in high vacuum, followed by

isolation of the intermediates and subsequent chemical analysis, IR spectroscopy, X-ray powder diffraction studies, Moessbauer spectroscopy, scanning electron microscopy, scanning Auger microprobe and mass spectroscopy.

Results and discussion

Thermal analysis of the above-mentioned hydrazidocarbonates was performed in an inert dry argon atmosphere or in vacuum for the preparation of the intermediates. Previous experiments revealed [18] that the thermal decomposition of the samples in an oxidizing atmosphere (air) usually leads to metal oxides with less pronounced or fewer intermediate stages.

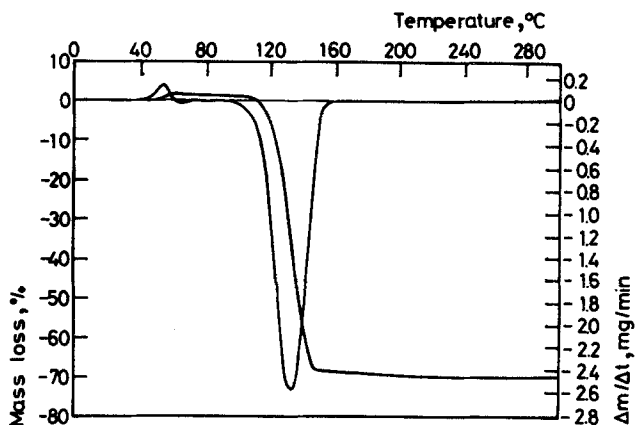


Fig. 2 TG and DTG curves for $\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$

Copper(II) hydrazidocarbonate semihydrate, $\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$, starts to decompose at 64°C in a dry argon atmosphere (Fig. 2). It decomposes in one step to the final product, elemental copper. Dehydration of the sample was not observed in the TG and DTG curves. Following the DTG peak at 134° the decomposition was completed at 241° . The calculated weight losses for decomposition of the sample to the metal and to copper(II) oxide are 71.44% and 64.25%, respectively. The observed weight loss and chemical analysis of the residue revealed that the end-product was elemental copper powder, which was oxidized to some extent.

Thermal decomposition of nickel(II) hydrazidocarbonate dihydrazine, $\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{N}_2\text{H}_4$, starts at 192° , with a DTG peak at 218° , accompanied by a strong exotherm (Fig. 3). In the first step, it loses 72.5% of its initial weight, and with increasing temperature it loses another 1.45%. The decomposition is finished at 353° , with a cumulative weight loss of 73.95%, which does not correspond to a net decomposition to elemental nickel, with a calculated weight loss of 78.48%. These results indicate that the reduction to nickel was not complete.

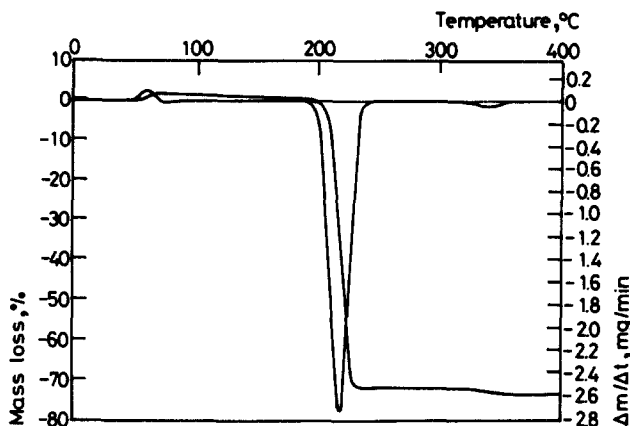


Fig. 3 TG and DTG curves $\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{N}_2\text{H}_4$

During the study of the thermal properties of hydrazinium(1+) tris-hydrazidocarbonateferrate(II) monohydrate, $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$, it became clear that iron(II) hydrazidocarbonate, $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$, is just one of the intermediates through which the decomposition of this compound proceeds; this is discussed below. The initial temperature of the thermal decomposition when starting from iron(II) hydrazidocarbonate is rather low, i.e. 50° .

Hydrazinium(1+) tris-hydrazidocarbonateferrate(II) monohydrate, $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$, starts to lose weight at 98° (Fig. 4 and Table 3) and the decomposition proceeds through several stages. In the first step, dehydration of the monohydrate occurs, which is finished at 151° :



The second step, leading to iron(II) hydrazidocarbonate, starts at 151° and is completed at 218°:



Further increase in the temperature leads at about 300° to an intermediate with a cumulative weight loss of 72.3%. The composition of this intermediate has not yet been determined, but analysis by mass spectrometry of the evolved gases in the last decomposition step revealed the presence of a gas with a molar weight of 28, which could be either nitrogen or carbon oxide, and the weight loss of 4.3% corresponds to half a mole of this gas per mole of iron. The thermal decomposition of the sample is completed at 468°.

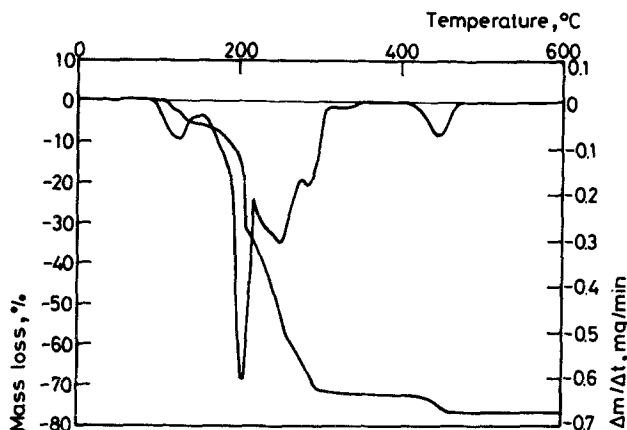


Fig. 4 TG and DTG curves for $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3]\cdot\text{H}_2\text{O}$

The thermal decomposition reactions of the complex compound $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3]\cdot\text{H}_2\text{O}$ were also followed by heating larger quantities of the sample (1 g) on a vacuum system connected to a mass spectrometer for analysis of the evolved components. Under these conditions, the decomposition started at 40° with the evolution of water vapour. At 60°, traces of carbon dioxide, ammonia and nitrogen could be detected in the evolved components. Up to 130°, the composition of the vapour phase was similar: 78% of water vapour, 10% of carbon dioxide, 6% of ammonia and the same amount of a component which could be either nitrogen or carbon monoxide

according to its molecular mass. Above 130°, the percentage of water diminished, accompanied by increases in the other components, giving a very reactive powder as an intermediate. Moessbauer spectroscopy demonstrated that most of the iron present in this is in the 2+ oxidation state. Although accurate chemical analysis on the content of carbon dioxide could not be performed due to the reactivity of the sample, the molar ratio of hydrazine to iron was 2 to 1 and the contents of both components complied with the formula $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$.

Table 3 Decomposition of $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3]\cdot\text{H}_2\text{O}$ in Ar

Decomp. step/r.	Temp. interval °C	Weight loss, %	
		calc.	found
I/2	98-151	5.63	5.4
II/3	151-218	31.33	29.6
III/4	218-300	-	37.3
IV/5	300-520	-	4.3

The investigation of the decomposition reactions, and the isolation and characterization of the intermediates were complicated by the extreme sensitivity of these products toward oxygen. When exposed to air, the intermediates and the end-products are pyrophoric and burn to the oxides. For thermoanalytical studies, the reactivity of these compounds demands very pure carrier gas, with an oxygen content of less than approximately 10 ppb. To achieve reliable chemical and other analyses, it is essential that air be rigorously excluded from the sample after its removal from the furnace. To determine the influence of the atmosphere on the composition of the end-product, the thermal analyses were carried out in different gases and in vacuo (Table 4), and the identity of the products was determined by powder diffraction measurements.

The end-product was iron powder oxidized to a greater or lesser degree. The calculated weight losses for decomposition of the hydrazidocarbonate to iron or its oxides are: Fe - 83.17, FeO - 78.35, Fe_3O_4 - 76.74 and Fe_2O_3 - 75.94%. The complete exclusion of air during the transfer of the samples from the furnace could not be achieved, and thus partial oxidation of the end-product could be the origin of this secondary oxidation. Comparison of the obtained and calculated weight losses of the sample during thermogravimetric analysis in an argon mixture containing 4% hydrogen revealed the good agreement between the observed and calculated weight

losses for decomposition to iron, but X-ray powder photography indicated the presence of Fe_3O_4 as well.

Table 4 The influence of the furnace atmosphere on the composition of the end product

Atmosphere	Weight loss, %	Product
Ar purified by oxi-sorb	76.6	Fe_3O_4
Ar without purification	78.1	Fe_3O_4
Ar mixture with 4% H_2	83.8	Fe, Fe_3O_4
Air	74.7	$\alpha\text{-Fe}_2\text{O}_3$
Vacuum	76.4	Fe, Fe_3O_4

In the literature, a thermal decomposition scheme has been proposed [21] for the decomposition of $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3]\cdot\text{H}_2\text{O}$. The first step is dehydration of the sample, leading to anhydrous $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3]$, followed by $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3$, which at higher temperatures decomposes to $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$, and finally to iron(III) oxide. Neither the composition of the furnace atmosphere nor other explicit data were given for the proposed scheme.

The thermal properties of the hydrazidocarbonates should be compared with those of similar compounds (Table 5).

Table 5 The initial and 1st DTG peak temperatures for the decomposition of the hydrazido-carbonates

Compound	T_1 , °C	T_2 , °C	DSC
$\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$	50	165	endo
$\text{Co}(\text{N}_2\text{H}_3\text{COO})_2$ (19)	240	330	endo
$\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2\cdot 0.5\text{H}_2\text{O}$	64	134	endo
$\text{Co}(\text{N}_2\text{H}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ (19)	100	188	endo
$\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ (19)	151	245	endo
$\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2\cdot \text{H}_2\text{O}\cdot \text{N}_2\text{H}_4$ (19)	105	220	exo
$\text{Co}(\text{N}_2\text{H}_3\text{COO})_2\cdot \text{N}_2\text{H}_4$ (19)	155	220	exo
$\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2\cdot 2\text{N}_2\text{H}_4$	192	218	exo
$\text{Co}(\text{N}_2\text{H}_3\text{COO})_2\cdot 2\text{N}_2\text{H}_4$ (19)	110	184	exo
$\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3]\cdot \text{H}_2\text{O}$	98	127	endo
$\text{N}_2\text{H}_5[\text{Co}(\text{N}_2\text{H}_3\text{COO})_3]\cdot \text{H}_2\text{O}$ (19)	115	166	endo
$\text{N}_2\text{H}_5[\text{Ni}(\text{N}_2\text{H}_3\text{COO})_3]\cdot \text{H}_2\text{O}$ (19)	130	211	endo
$\text{K}[\text{Co}(\text{N}_2\text{H}_3\text{COO})_3]$ (19)	230	290	exo

T_1 - the initial temperature

T_2 - the temperature of the first DTG peak

A comparison (Table 5) of the complex iron compound $N_2H_5[Fe(N_2H_3COO)_3].H_2O$ with the isostructural nickel and cobalt compounds of the same type, i.e. $N_2H_5[Ni(N_2H_3COO)_3].H_2O$ and $N_2H_5[Co(N_2H_3COO)_3].H_2O$ [19], demonstrates the increasing thermal stability sequence $Fe > Co > Ni$. In the latter compounds, thermal dehydration cannot be carried out since dehydration is accompanied by decomposition of the samples. With cobalt and nickel, the second step of decomposition leads to $M(N_2H_3COO)_2.N_2H_4$ ($M = Co, Ni$) instead of the $M(N_2H_3COO)_2$ obtained for $M = Fe$. The reason is the greater stability of $Fe(N_2H_3COO)_2$ as compared to $Fe(N_2H_3COO)_2.N_2H_4$, which to our knowledge has not yet been isolated by other methods. The disproportionation of the hydrazine present in the coordination sphere of the cation is the cause of the intense exotherms in the thermal decomposition reactions of the hydrazidocarbonates of the type $M(N_2H_3COO)_2.nN_2H_4$ (Table 5).

Conclusion

The hydrazidocarbonates studied in this paper exhibit similar thermal properties to those of other compounds of the same type. The main difference is in the thermal stability of these compounds and some intermediates, where the influence of the central cation displays an important role. The end-products are to a greater or lesser extent oxidized metals. The reduction of the metals is the result of direct reduction of the central cations by the hydrazidogroup, hydrazine or their decomposition products. The composition of the end-product depends on several factors: the purity and the flow rate of the carrier gas, the geometry of the crucible and the sample in it, the residence time and concentration of evolved gases in the crucible, and the sample weight.

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Zusammenfassung — In einer inerten Argonatmosphäre wurden die thermischen Eigenschaften einiger Hydrazidocarbonate von Kupfer, $\text{Cu}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$, Nickel $\text{Ni}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{N}_2\text{H}_4$ und Eisen $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2$ bzw. $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$ ermittelt, d.h. TG-, DTG- und DSC-Kurven wurden angefertigt. Im Falle von $\text{N}_2\text{H}_5[\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$ konnten während der Zersetzung auch Zwischenprodukte beobachtet und isoliert werden. Die Endprodukte waren mehr oder weniger oxydierte Metallpulver.