

Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF $M(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($M=\text{Cu}, \text{Co}, \text{Ni}$)

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Abstract

This paper presents the results of simultaneous DTA–TG–DTG and DSC studies on the thermal decomposition of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in an air atmosphere. The mechanism and enthalpies of the investigated processes were determined, as well as the kinetic parameters of the processes run under non-isothermal conditions by means of Kissinger's method. The dependence of the activation energy on the ionic radius of the cations building up the crystal lattices of the investigated compounds was also studied.

Keywords: kinetics, nitrates, thermal decomposition

Introduction

The thermal decomposition of hydrated nitrates has been investigated by many authors [1–6], whose results were summarized by Liptay in the well known 'Atlas of Thermoanalytical Curves' [7]. The dominant opinion is that at temperatures lower than 100°C , $M(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ partially dehydrates and melts in the rest of the non-dehydrated material during the thermal decomposition [1–5]. In the latter stage of the process a complete dehydration takes place, then the nitrates decompose forming the oxides, which are the final product of dehydration [6]. Such a mechanism has been determined by means of DTA and TG methods for numerous hydrated nitrates [7].

Recently Wojciechowski *et al.* [8–10] have determined the mechanism of thermal decomposition of $\text{Cr}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ by means of DTA and TG technique, but the obtained mechanisms are different for the three investigated cases.

This paper presents the results of studies on the thermal decomposition of $M(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$, ($M=\text{Cu}, \text{Ni}, \text{Co}$) compounds, obtained by using simultaneous

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DTA–TG–DTG technique and DSC method at different heating rates in an air atmosphere. The kinetics, mechanism and enthalpies of the processes and the specific heats of the products formed during the thermal decomposition were determined.

Experimental

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ produced by Merck (p.a. purity) were used in the experiments.

The thermoanalytical equipment used for the experimental work was a Derivatograph (1500°C) (MOM, Budapest, Hungary), and a high-temperature DSC-404 (Netzsch, Germany). All measurements were carried out in a static air atmosphere. The sample mass was 300 mg for the DTA–TG–DTG measurements and 20 mg for the DSC measurements.

Results and discussion

Comparative DTA–TG–DTG investigations at heating rates of 2.5; 5; 10 and 20°C min⁻¹ were done in an air atmosphere, and the results obtained at a heating rate of 5°C min⁻¹ are shown in Fig. 1 for $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in Fig. 2 for $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and in Fig. 3 for $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Comparative analysis of the results shown in Figs 1–3, indicates that the same mechanism is involved in all three cases. Four endothermic processes, accompanied by mass loss, correspond to the complete dehydration and thermal decom-

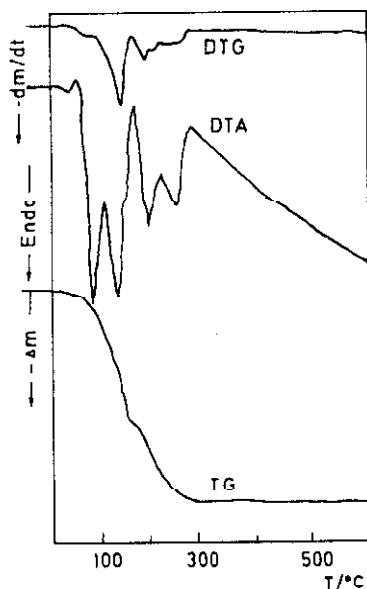


Fig. 1 DTA–TG–DTG curves of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in an air atmosphere at a heating rate of 5°C min⁻¹

position of the nitrates and as a result, stable oxides are formed at temperatures higher than 330°C in all three cases.

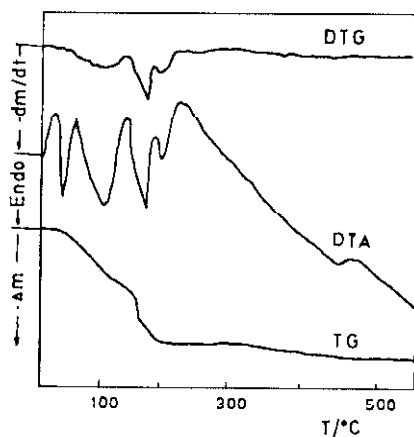


Fig. 2 DTA–TG–DTG curves of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in an air atmosphere at a heating rate of 5°C min^{-1}

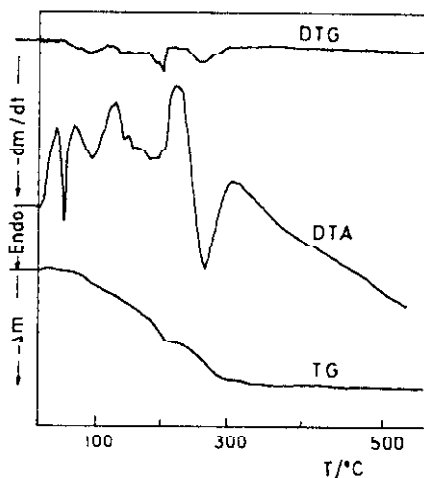
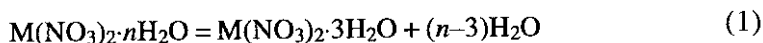


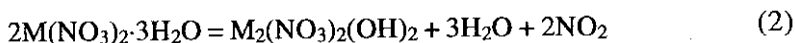
Fig. 3 DTA–TG–DTG curves of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in an air atmosphere at a heating rate of 5°C min^{-1}

For the investigated heating rate interval from 2.5 to $20^\circ\text{C min}^{-1}$, the following mechanism of the processes can be proposed, based on the results of DTA–TG–DTG measurements:

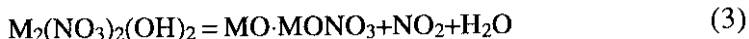
The first process in the temperature range of 40 – 90°C is the melting of the compounds and partial dehydration:



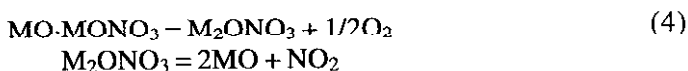
The second process in the temperature range of 110–150°C:



The third process in the temperature range of 170–220°C:



The fourth process in the temperature range of 280–320°C:



where $M = \text{Cu}$, Co and Ni .

The DSC curves of the compounds studied at a heating rate of $10^\circ\text{C min}^{-1}$ are shown in Fig. 4. It is obvious that the same processes were registered as by the DTA curves (Figs 1–3). The enthalpies of the processes were determined based on DSC measurements in a static air atmosphere, and are presented in Table 1.

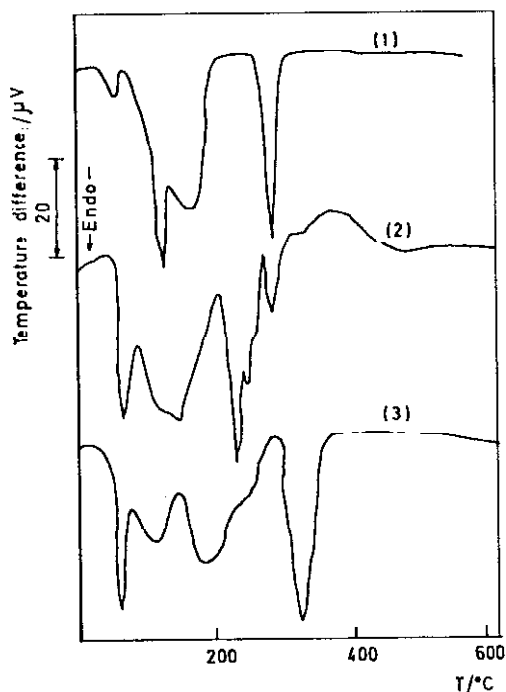


Fig. 4 DSC curves of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3) in an air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$

Table 1 Enthalpy values of the thermal decomposition of $M(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$, ($M=\text{Cu, Ni, Co}$)

Compound	Enthalpy/ J g^{-1}			
	1st process	2nd process	3rd process	4th process
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	14.7	84.9	158	196
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	77.8	276	204	21
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	85	86.3	375	286

From the DTA results obtained at different heating rates (2.5; 5; 10 and $20^\circ\text{C min}^{-1}$), the kinetic parameters of the processes were determined by means of Kissinger's method [11]:

$$\ln \frac{\theta}{T_m^2} = C - \frac{E_a}{RT_m}$$

where: θ – heating rate (K min^{-1}), T_m – the peak temperature on the DTA curve (K), R – gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), E_a – activation energy of the process (kJ mol^{-1})

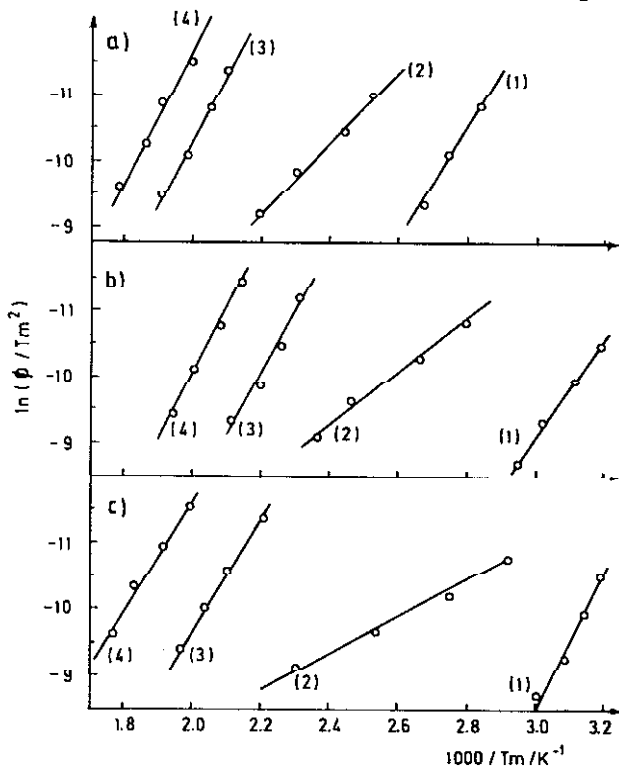


Fig. 5 Dependence $\ln(\theta/T_m^2)=f(1/T_m)$ for the thermal decomposition processes of a) $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; b) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; c) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

and C – integration constant. The activation energies of the investigated processes determined from the dependence $\ln(\theta/T_m^2)=f(1/T_m)$ shown in Fig. 5, are presented in Table 2.

Table 2 Activation energies of the thermal decomposition processes of $M(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($M=\text{Cu, Co, Ni}$)

Compound	Activation energy/ kJ mol^{-1}			
	1st process	2nd process	3rd process	4th process
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	159	50	190	298
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	137	6	205	344
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	171	21	59	96

The compounds studied ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) have similar ionic crystal structures, which is the reason for the similarity in the mechanisms and kinetic parameters for the processes occurring during their thermal decomposition. The only difference is that the ionic radius of the Ni^{2+} cation is smaller than those of the Cu^{2+} and Co^{2+} , cations which build up the crystal lattices of the investigated compounds [12].

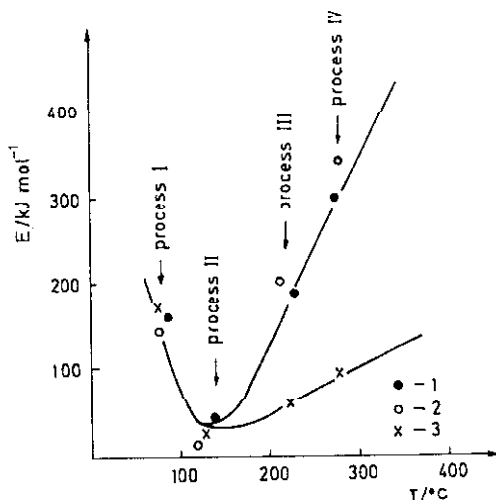


Fig. 6 Dependence of the activation energy on the temperature for the thermal decomposition processes of: 1 – $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; 2 – $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 3 – $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

The dependence of the obtained activation energy values on the temperature is shown in Fig. 6. The Figure shows that the first process, involving the melting and partial dehydration of $M(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($M=\text{Cu, Co, Ni}$), takes place in the kinetic area, so that the temperature has a dominant influence on the rate of the

process. The second process, in which the original structure is broken and a new one, of the type $M_2(NO_3)_2 \cdot (OH)_2$ is formed, obviously has a diffusion character if one has in mind the relatively low values of the activation energy. The activation energy values obtained for the first and second process are close to each other. At higher temperatures, for the third and fourth process, the activation energy values are almost the same for $Cu_2(NO_3)_2(OH)_2$ and $Co_2(NO_3)_2(OH)_2$, while for $Ni_2(NO_3)_2(OH)_2$ they are much lower. The reason for this may be that in the hydroxonitrates the Cu^{2+} and Co^{2+} cations have the same ionic radii ($0.72 \cdot 10^{-10}$ m), while the ionic radius of the Ni^{2+} cation is smaller ($0.69 \cdot 10^{-10}$ m).

It is obvious that the smaller ionic radius of Ni enables a more compact packing of the $Ni_2(NO_3)_2(OH)_2$ lattice related to the lattices of the same type, where Cu^{2+} and Co^{2+} occur as cations with larger ionic radius. This may influence the repulsive forces in the presence of Ni, because the interatomic distance is decreasing and thus the values determined for the activation energies of the third and fourth process are smaller than those for the systems containing Cu and Co. For the compounds containing cations of the same ionic radius (Cu^{2+} and Co^{2+}), in the crystal lattice, approximately same values were obtained for E_a for the third and fourth process (the differences may be due to experimental and calculation errors).

References

- 1 W. W. Wendlandt, *Anal. Chim. Acta*, 15 (1956) 435.
- 2 W. W. Wendlandt and J. L. Bear, *J. Inorg. Nucl. Chem.*, 12 (1960) 276.
- 3 M. Dabkowska and A. Broniszewska, *Annales Univ. Mariae Curie Skłodowska, Lublin Sectio, AA* 28 (1973) N°12.
- 4 M. Dabkowska, *Annales Univ. Mariae Curie Skłodowska, Lublin Sectio, AA* 29 (1974) N°5.
- 5 D. M. Dvornikova, W. P. Sevostianov and N. M. Ambrozhi, *Zh. Neorg. Khim.*, 14 (1969) 2325.
- 6 D. M. Chizikov, B. N. Rabinovich and E. H. Subbotina, *Zh. Neorg. Khim.*, 10 (1965) 2527.
- 7 G. Liptay, *Atlas of Thermoanalytical Curves*, Akadémiai Kiadó, Budapest 1976.
- 8 K. Gajerski, S. Labus, A. Malecki and K. T. Wojciechowski, *Proc. CETTA'97, Zakopane 8-13 September 1997, Abstracts*, p. 309.
- 9 K. T. Wojciechowski, R. Gajerski, S. Labus and A. Malecki, *Proc. CETTA'97, Zakopane 8-13 September 1997, Abstracts*, p. 79.
- 10 K. T. Wojciechowski, R. Gajerski, S. Labus and A. Malecki, *Proc. CETTA'97, Zakopane 8-13 September 1997, Abstracts*, p. 80.
- 11 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 12 A. Kelly and G. W. Groves, *Crystallography and Crystal Defects*, Longman, London 1970, p. 472.