MECHANISM OF THERMAL DECOMPOSITION OF *d*-METALS NITRATES HYDRATES

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Abstract

A series of six nitrates(V) hydrates of 4*d*-metals as well as mercury and cadmium thermal decomposition was examined by DTA, TG and EGA techniques. It was found that thermal decomposition of *d*-metals nitrate(V) hydrates proceeds in three stages: partial dehydration, oxo-nitrates and hydroxide nitrates formation and metal oxides formation. General chemical equations for all decomposition stages were proposed. It was found that dehydration of hydrated salts is accompanied by partial decomposition of nitrate(V) groups.

Keywords: DTA, EGA, *d*-metals, nitrates, thermal decomposition

Introduction

d-Metal nitrates hydrates are the class of substances commonly used for preparation of high surface area materials. From this point of view the detail microscopic mechanism as well as the kinetics of thermal decomposition of these salts is important to know. There are some reports concerning decomposition of nitrates but general mechanism of this process has not been found so far [1–3].

The goal of the work undertaken in our laboratory is to find regularities concerning these reactions. In the study reported here, a series of six nitrates(V) hydrates of 4*d* metals as well as mercury and cadmium were investigated. Special attention will be paid to the influence of cation ability to change its oxidation state on the mechanism of thermal decomposition.

Experimental

Results presented in this work are based on earlier investigations on decomposition of $Cr(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 2H_2O$ and $Ni(NO_3)_2 \cdot 2H_2O$ [4, 5]. Additionally preliminary investigations on decomposition of the following nitrates were made: $Fe(NO_3)_3 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Hg(NO_3)_2 \cdot nH_2O$ [6–8]. Compounds used in experiments were commercial, pure for analysis.

Studies of thermal decomposition processes were pursued using thermogravimetric analysis (TG) and differential thermal analysis (DTA) on SDT 2960 TA INSTRUMENTS and evolved gas analysis (EGA) of volatile products with quadrupole mass spectrometer QMS ThermoStar by Balzers. The QMS was operated with electron energy of 700 eV.

Additionally, nitrate oxides evolved during decomposition were oxidized by ozone, then absorbed in solution and analyzed as nitrate ions using ion-selective electrode.

Solid products of decomposition were identified by X-ray diffraction analysis as well as by chemical analysis (gravimetric and volumetric). Absorption spectrophotometry was used to determine a ratio of metal ion contents in different oxidation states.

Results and discussion

It is characteristic of all studied metal nitrates that they crystallize from water solutions as ionic hydrates and that their dehydration cannot be achieved by heating, because dehydration proceeds together with partial decomposition of nitrate groups. The only exception is cadmium nitrate hydrate. Two causes of this can be pointed out.

Nitrate ion NO_3^- has got flat crystallographic structure, with three-fold axis of symmetry, which goes through the metal atom and is perpendicular to the nitrate ion plane. In the simplest case oxygen in NO_3^- has formal charge equal 1/3 elementary charge unit. For small cations of *d*-metals, the typical configuration in the crystallographic lattice of nitrates(V) with coordination number 6 provides neutralization of cation charge at its oxidation state equal +2. In this case anhydrous nitrates could be obtained by thermal dehydration. In fact, it is possible only for $Cd(NO_3)_2$, other discussed nitrates can be produced only by synthesis in non-water medium [9].

For the present, the crystallographic structure of the anhydrous nitrates(V) under discussion is not known in detail though they are supposed to form van der Waals crystals in solid state. If so, producing anhydrous salts by dehydration require complete reconstruction of crystallographic lattice accompanied by partial decomposition of nitrate(V) ions.

For small cations with oxidation state higher than +2, the coordination number required for neutralization of electric charge by nitrate(V) ions (with formal charge on oxygen equal 1/3) is too high in respect to geometrical conditions, such as is not noticed in real compounds. This geometric problem vanishes if we consider hydration of cation which leads to formation of large ion $M(H_2O)_n^{k+}$ ($k>2$) with electric charge spread on its surface. The hydrated ion can coordinate adequate number of nitrate(V) ions to neutralize M^{k+} charge. In that case dehydration of metal nitrate(V) hydrate proceeds with partial decomposition of nitrate(V) ions.

Formally also alternate structure of NO_3^- ion exists which allows formation of anhydrous nitrates(V). In this structure two oxygen ions have formal electric charge equal 1/2 and the whole nitrate(V) ion acts as bidentate or bridge ligand. With such a structure, high coordination number must not realize neutralization of charge of structure unit. However anhydrous metal nitrates(V) which exhibit this alternate

structure of NO_3^- ion form rather van der Waals crystals in solid state. Thus the mechanism of dehydration with changing NO_3^- ion structure from this with electric charge uniformly distributed on oxygen ions to that with electric charge equal 1/2 only on two oxygen ions is unlikely.

Another cause of forming hydrates by *d*-metals nitrates(V) is their ability to form aqua-complexes $[M(H_2O)_p]^{m+}$ in water solutions. Thus the correct formula of hydrated nitrate(V), $M(NO_3)_m \cdot nH_2O$, should be as follows: $[M(H_2O)_p](NO_3)_m \cdot (n-p)H_2O$. This notation shows that in the single molecule of salt differently bounded water molecules (semipolar, van der Waals and hydrogen bond) can exist, the consequence of which is that dehydration proceeds by stages.
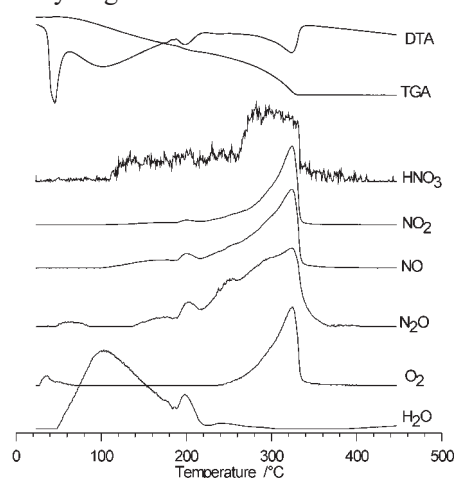

Fig. 1 Non-isothermal decomposition of $Zn(NO_3)_2 \cdot 6H_2O$ (in helium, $\beta = 5°C \ min^{-1}$)

Figure 1 shows typical TG and DTA curves for *d*-metals nitrates(V) hydrates decomposition by example of $Zn(NO_3)_2 \cdot 6H_2O$.

Results obtained show that the first stage of thermal decomposition of nitrates(V) hydrates under investigation is partial dehydration frequently preceded by melting:
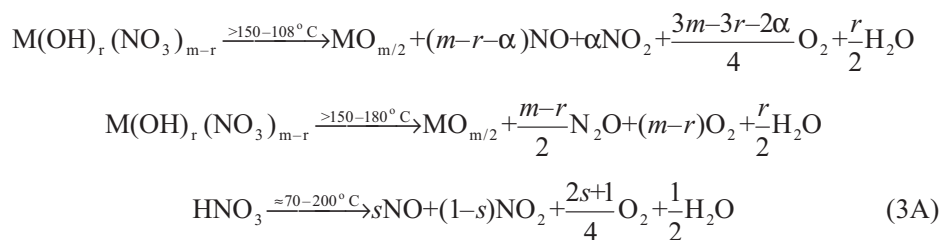
$$M(NO_3)_m \cdot nH_2O \xrightarrow{30-60°C} M(NO_3)_m \cdot (n-q)H_2O + qH_2O \qquad (1)$$
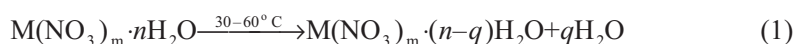
and $(n-q) \ 2$ (only for cadmium nitrate(V) $(n-q)=0$). In the next stage decomposition proceeds with further dehydration accompanied by decomposition of nitrate(V) ions. The image of this phenomenon depends on the cation nature, first of all on its ability to undergo oxidation. If cation can not be oxidized (e.g. Fe^{3+} or Zn^{2+}), the second stage of nitrates(V) decomposition leads to formation of nitrates(V) hydroxides according to the following scheme:

$$M(NO_3)_m \cdot (n-q)H_2O \xrightarrow{\approx 60-180°C} M(OH)_r(NO_3)_{m-r} + rHNO_3 + (n-q-r)H_2O \qquad (2A)$$

In fact (n–q) moles of H_2O means only summary content of water in the molecule, not only crystallization water but also water bounded by van der Waals forces.
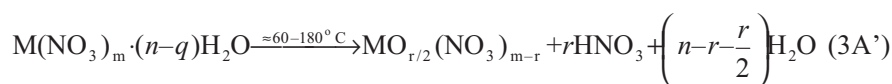
In Fig. 1 it can be noticed that increasing of H_2O signal corresponds to appearing of HNO_3 signal. On DTA curve, below 50°C an endothermic effect can be observed without a change of mass on TG curve corresponding to melting of the sample. Formation of metal hydroxides nitrates(V) accompanied by dehydration solves the problem of neutralization of cation charge by surrounding anions discussed before. Formal charge on oxygen atom in OH group is –1 in respect to –1/3 in nitrate(V) ion. Analogous situation occurs during $Fe(NO_3)_3 \cdot 6H_2O$ thermal decomposition.

In the third stage of decomposition of $M(NO_3)_m \cdot nH_2O$ when M^{m+} cannot be oxidized, degradation of NO_3^- groups occurs in both those connected to cation and those from HNO_3, formed in the second stage of decomposition. Degradation proceeds with formation of NO, NO_2, N_2O and O_2. NO, NO_2 and O_2 were reported as decomposition products in previous works, but significant amount of N_2O observed in present investigations has not been reported yet. Generally, reactions in third decomposition stage can be written as:

$$M(OH)_r(NO_3)_{m-r} \xrightarrow{>150-108^\circ C} MO_{m/2} + (m-r-\alpha)NO + \alpha NO_2 + \frac{3m-3r-2\alpha}{4}O_2 + \frac{r}{2}H_2O$$

$$M(OH)_r(NO_3)_{m-r} \xrightarrow{>150-180^\circ C} MO_{m/2} + \frac{m-r}{2}N_2O + (m-r)O_2 + \frac{r}{2}H_2O$$

$$HNO_3 \xrightarrow{\approx 70-200^\circ C} sNO + (1-s)NO_2 + \frac{2s+1}{4}O_2 + \frac{1}{2}H_2O \qquad (3A)$$

In reactions (3A) two parallel processes of conversion of nitrate(V) ion were taken into account because formation NO, NO_2 and N_2O seems to be unlikely in respect to N–N bond existing in N_2O but absent in other nitrogen oxides.

When cation M^{m+} can not be oxidized (e.g. Fe^{3+}) during the reaction and $m>2$, oxo-nitrates can be formed in the second stage of decomposition of *d*-metal nitrates(V), besides hydroxides nitrates:

$$M(NO_3)_m \cdot (n-q)H_2O \xrightarrow{\approx 60-180^\circ C} MO_{r/2}(NO_3)_{m-r} + rHNO_3 + \left(n-r-\frac{r}{2}\right)H_2O \quad (3A')$$

Oxo-nitrates decompose to oxides like hydroxide nitrates do. It is worth to emphasize that this way of decomposition provides easy neutralization of cation charge in the lattice for O^{2-} ion appears.

The mechanism of nitrates decomposition described above changes when cation M^{m_1+} can become oxidized to M^{m_2+}. Good examples of this can be decomposition of $Co(NO_3)_2 \cdot 2H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ (Figs 2 and 3). The first stage of decomposition of this type nitrates is analogous to mechanism of decomposition of nitrates described above with cations which can not change their oxidation state. The second stage is more complex than reaction (2A) and consists of additional reactions of electron
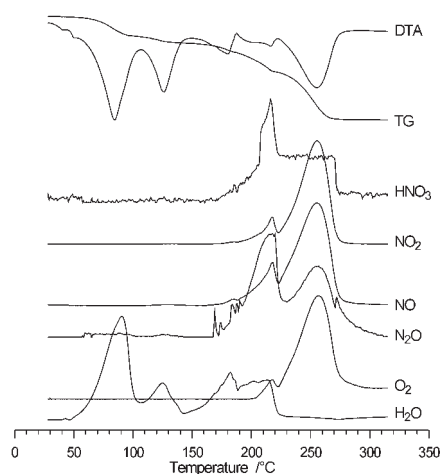
Fig. 2 Non-isothermal decomposition of $Co(NO_3)_2 \cdot 2H_2O$ (in helium, $\beta=5°C\ min^{-1}$)
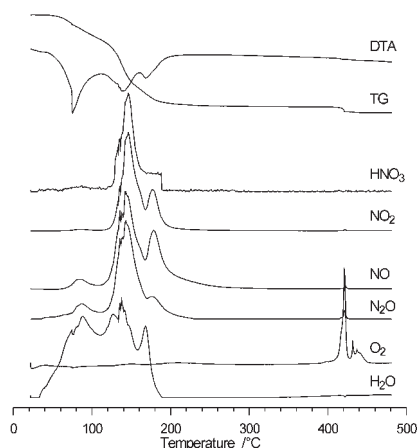
Fig. 3 Non-isothermal decomposition of $Cr(NO_3)_2 \cdot 9H_2O$ (in helium, $\beta=5°C\ min^{-1}$)

transport between anionic and cationic sub-lattice resulting in oxidation of cation and reduction of nitrates(V) groups. Generally, it can be written as:

$$MNO_3)_{m_1} \cdot (n-q)H_2O \xrightarrow{\approx 60-180°C} M_{1-x}^{m_1+} M_x^{m_2+} O_y (OH)_z (NO_3)_v +$$

$$\alpha NO + \beta NO_2 + (m_1 - v - \alpha - \beta)HNO_3 + \left(n - q - \frac{z + m_1 - v - \alpha - \beta}{2} \right) H_2O \qquad (2B)$$
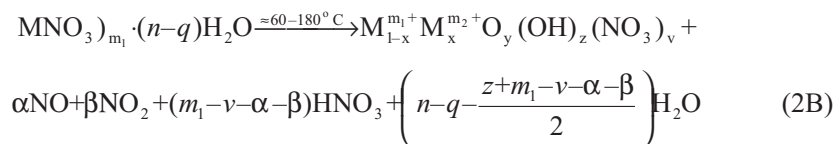
A feature characteristic of the reaction (2B) is a lack of oxygen in the products of reaction. Elemental oxygen appears only in the third stage, in which further decomposition of oxo-nitrates and hydroxide nitrates(V) occurs, according to one of two possible reaction schemes:

$$M_{1-x}^{m_1+}M_x^{m_2+}O_y(OH)_z(NO_3)_v \xrightarrow{>120-150^{\circ}C}$$

$$M_{1-x'}^{m_1+}M_{x'}^{m_2+}O_y+\alpha'NO+\beta'NO_2+\gamma'O_2+\delta'H_2O$$

$$M_{1-x}^{m_1+}M_x^{m_2+}O_y(OH)_z(NO_3)_v \xrightarrow{>120-150^{\circ}C}$$ (3B)

$$MO_{m_1/2}+\alpha''NO+\beta''NO_2+\gamma''O_2+\delta''H_2O$$

$$...+\alpha''NO+\beta''NO_2+\gamma''O_2+\delta''H_2O$$
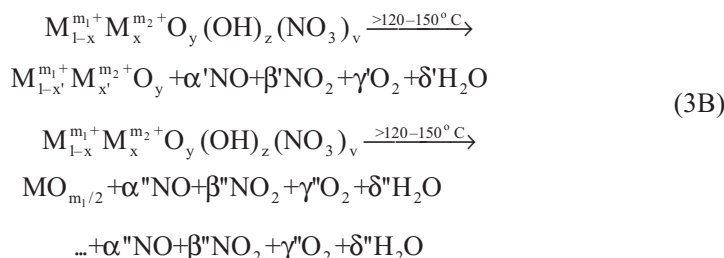
Another parallel way of reaction leading to formation of N_2O instead of NO and NO_2 is also observed. It is possible too, that in third stage, along with reactions (3B), the following reaction takes place:

$$M_{1-x'}^{m_1+}M_{x'}^{m_2+}O_{y'} \xrightarrow{>150^{\circ}C} MO_{m_1/2}+\left(\frac{y'}{2}-\frac{m_1}{4}\right)O_2$$ (3B')
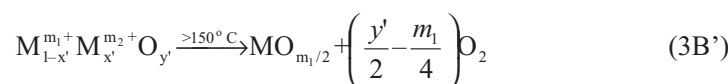
Some oxygen is formed during thermal decomposition of HNO_3 like it is in case of $Co(NO_3)_2 \cdot 2H_2O$ decomposition (Fig. 2). This is not the case for $m_1>2$, when oxygen does not arise (or amount of oxygen is so small that hard to detect). If there is no oxygen in decomposition products but HNO_3 is present, reaction proceeds through oxidation of M^{m_1+} to M^{m_2+} and NO_3^- ions are reduced without elemental oxygen liberation. This can be illustrated by comparison of thermal decomposition of cobalt nitrate(V) hydrates and chromium nitrate(V) hydrates given in Figs 2 and 3.

The above presented series of chemical equations corresponding to thermal decomposition of d-metals nitrate hydrates gives general view of reactions occurring during the process of decomposition. However, a few questions remain without answers:

1. Is formation of both NO and NO_2 a consequence of two different processes which NO_3^- ion being in one configuration undergoes or is it a result of processes which undergo NO^- ions being in different configuration?

2. What determines the $[NO]/[NO_2]$ ratio? It is only known that $[NO]/[NO_2]$ depends somehow on the way the decomposition is carried out and the thermal history of the sample investigated.

3. Another question concerns the mechanism of N–N bond creation while N_2O is formed? It seems that formation of N_2O is only slightly dependent on the cation of the decomposed nitrate. Is N_2O a product of reaction between nitrate ions: $2NO_3^- \rightarrow N_2O+2O_2+O^{2-}$? If so, oxidation of cation cannot be related to N_2O formation.

4. The basic question remains without answer: what is a reason of lowering thermal stability of NO_3^- ion in d-metals nitrates(V) in relation to alkali metals nitrates(V). For instance, KNO_3 even at 600°C does not exhibit any decomposition symptoms. May be the cause is that NO_3^- ions are the ligands in complex ions $[M(H_2O)_a(NO_3)_b]^{(m_1+b)+}$ or that a hydrogen bond exists in hydrates $H..ONO_2$. The answer can be connected with the role of d-electrons in the mechanism of thermal decomposition of nitrates(V) hydrates.

A full set of results concerning mechanism of thermal decomposition of all d-metal nitrates(V) hydrates can give the answers to these questions.

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