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Formation of N_2O during thermal decomposition of *d*-metal hydrates nitrates

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Abstract

It was found that during thermal decomposition of hydrates of *d*-metal nitrates nitrous oxide (N_2O) is always present among the other gaseous products: H_2O, HNO_3, NO, NO_2 and O_2. In all studied decomposition reactions the nitrous oxide formed contains approximately 5–8% of total nitrogen coming from nitrate. Two new mechanisms of N_2O formation, based on the reaction between NO or NO_2 and nitrate ion, have been proposed. The discussed third possible mechanism: (a) $2NO = N_2O_2$ and (b) $N_2O_2 + NO = N_2O + NO_2$ is unlikely.

Keywords: Thermal decomposition; *d*-Metal nitrate; Nitrous oxide

1. Introduction

Generally thermal decomposition of *d*-metal hydrates nitrates can be described by the following equation [1]:

$$\mathrm{Me(NO_3)_n \cdot qH_2O \xrightarrow{heating} Me_xO_y + (HNO_3, NO, NO_2, O_2, H_2O)} \quad (1)$$

The whole process of decomposition consists of several consecutive reactions which were published in [2] in the form of scheme given in Fig. 1. The mutual ratio of gaseous products: HNO_3, NO, NO_2, O_2 and H_2O, depend on the metal nitrate as well as on the experimental conditions of decomposition (i.e. mass of the sample, heating rate, gas over decomposing sample).

The degradation of NO_3^- ions proceeds according to the following formal equation:

$$\mathrm{NO_3^- \rightarrow} x\mathrm{NO} + (1-x)\mathrm{NO_2} + \frac{2x+1}{4}\mathrm{O_2} + \frac{1}{2}\mathrm{O^{2-}} \quad (2)$$

The oxidation state of metal Me in oxide Me_xO_y is the same as in metal nitrate only when cation Me^{n+} can not be oxidized (for example, Zn^{2+} or Cd^{2+}). Otherwise, cation Me^{n+} oxidizes to $Me^{n'+}$, what can be described by the total equation:

$$\mathrm{Me^{n+} + NO_3^- \rightarrow Me^{n'+}} + y\mathrm{NO} + (1-y)\mathrm{NO_2} + \left(\frac{1+2y-\Delta n}{4}\right)\mathrm{O_2} + \left(\frac{\Delta n+1}{2}\right)\mathrm{O^{2-}} \quad (3)$$

where $\Delta n = n' - n > 0$.

In fact, due to low probability of direct electron transport from cation to anion, Eq. (3) should be considered as a sum of elementary reactions. One elementary reaction is degradation of NO_3^- described by Eq. (2) and the second—oxidation of Me^{n+} described by Eq. (4):

$$\mathrm{Me^{n+}} + \frac{\Delta n}{4}\mathrm{O_2} \rightarrow \mathrm{Me^{n'+}} + \frac{\Delta n}{2}\mathrm{O^{2-}} \quad (4)$$

Thus, the oxidation of metal cation is a result of a secondary process in which oxygen produced during NO_3^- degradation takes part. For instance, decomposition of $Ni(NO_3)_2$ in inert atmosphere (Ni^{2+} does not change its oxidation state) is described by the summary equation:

$$\mathrm{Ni(NO_3)_2 \rightarrow NiO} + y\mathrm{NO} + (2-y)\mathrm{NO_2} + \frac{1+y}{2}\mathrm{O_2}$$

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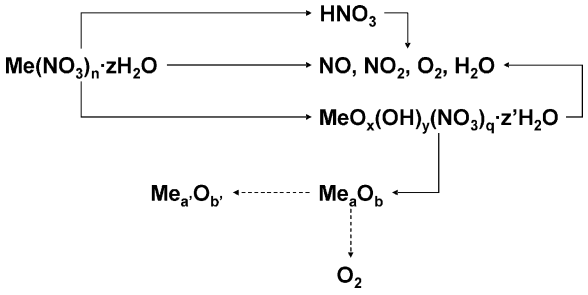

Fig. 1. The main routes of thermal decomposition of hydrates of nitrates of *d*-electron metals.

while decomposition of $Mn(NO_3)_2$ in inert atmosphere (Mn^{2+} changes its oxidation state) is given by the following equation:

$$Mn(NO_3)_2 \rightarrow MnO_2 + yNO + (2-y)NO_2 + \tfrac{y}{2}O_2$$

Unfortunately a significant number of papers devoted to thermal decomposition of metal nitrates present results obtained either without the analysis of gaseous products of decomposition or with the analysis of only main gases. The usefulness of those results is limited from the point of view of determination the reaction routes.

In this paper we show that, besides HNO_3, NO, NO_2, O_2 and H_2O also nitrous oxide, N_2O, is present among gaseous products of *d*-metal nitrates decomposition. N_2O formation was not discussed in earlier papers devoted to *d*-metal nitrates decomposition. Only in paper [3], N_2O is mentioned among gaseous products of $Mn(NO_3)_2$ decomposition. The mechanism of N_2O formation will be discussed.

2. Experimental

All the experiments concerning thermal decomposition of hydrates of nitrates of different metals were carried out with commercial compounds in wide range of experimental conditions taking into account isothermal and non-isothermal measurements (heating rates varied in the range 0.1–20 K min^{-1}), mass of the samples (1–20 mg), gaseous atmosphere surrounding decomposing samples (helium, synthetic air with control of humidity). During measurements TGA and DTA signals were recorded (SDT 2960 TA INSTRUMENTS) simultaneously with MS spectra of gaseous products of decomposition using quadrupole mass spectrometer QMS 300 Thermostar, Balzers. The *m*/*z* values (*m*—molar mass of X^{z+} ion, *z*—charge of the ion) for which the ionic currents were recorded by mass spectrometer as well as the species corresponding to individual *m*/*z* are collected in Table 1.

The resolution of quadrupole mass spectrometer is approximately equal to 1 amu, thus the ionic current $I_{m/z} = I_{44}$ can correspond to N_2O^+ and as well to CO_2^+. It is necessary to remember that before measurement the samples had contact with CO_2 always present in atmosphere and small amount of it could be absorbed by the sample. Due to very high sensitivity of mass spectrometer this CO_2 is detected during the analysis of evolving gases thus the total ionic current I_{44} is the sum of the currents coming from CO_2 and N_2O: $I_{44} = I_{CO_2^+} + I_{N_2O^+}$.

Table 1
m/*z* with corresponding ions

m/*z*	Ion
12	C^+
14	N^+, N_2^{2+}
16	O^+, O_2^{2+}
17	OH^+
18	H_2O^+
28	CO^+, N_2^+
30	NO^+
32	O_2^+
44	CO_2^+, N_2O^+
46	NO_2^+
63	HNO_3^+

To distinguish between $I_{CO_2^+}$ and $I_{N_2O^+}$ the ionic current I_{12} was recorded. The ionic current I_{12} of C^+ which is a result of fragmentation of CO_2 molecule during its ionization by electron beam in mass spectrometer can be used to extract the signal of CO_2 from the total current I_{44}. When energy of electrons which ionized CO_2 molecule is 0.16 aJ (70 eV—standard in mass spectrometry) then the ratio $I_{C^+}/I_{CO_2^+}$ is 0.025 [8]. This value for our spectrometer was confirmed by independent measurements. Taking this into account the ionic current $I_{N_2O^+}$ can be calculated as:

$$I_{N_2O^+} = I_{44} - \frac{I_{C^+}}{0.025} \quad (5)$$

3. Results and discussion

The detailed TG/DTA/EGA-MS studies of thermal decomposition of several hydrates of *d*-metal nitrates: $Cr(NO_3)_3{\cdot}9H_2O$ [4], $Zn(NO_3)_2{\cdot}6H_2O$ [5], $Mn(NO_3)_6{\cdot}6H_2O$ [2], $Co(NO_3)_2{\cdot}6H_2O$ [6], $Ni(NO_3)_2{\cdot}6H_2O$ [2,7], $Hg_2(NO_3)_2$ [9], $Hg(NO_3)_2$ [9] carried out by us showed that nitrous oxide N_2O is always observed among gaseous products together with HNO_3, NO, NO_2, O_2 and H_2O. For all studied nitrates nitrous oxide contains approximately 5–8% of total nitrogen coming from nitrate. It is necessary to emphasize, that formation of N_2O during thermal decomposition is characteristic not only for hydrates of *d*-metal nitrates. N_2O was observed by us as a product of decomposition of $NaNO_3$, $Ca(NO_3)_2$, $Al(NO_3)$, etc. [9]. Fig. 2. presents ionic currents of chosen gaseous products (NO, N_2O and O_2) recorded during thermal decomposition of mentioned *d*-metal nitrates. An example of N_2O formation during thermal decomposition of *p*-metal nitrate, $Al(NO_3)_3{\cdot}6H_2O$, was showed as well. For clarity we do not present ionic currents for NO_2. It is enough to remember that the course of $I_{NO_2^+}$ with temperature is nearly the same as for I_{NO^+} and differences between those two currents concern the values not the shape.

It seems that the general scheme of thermal decomposition of $Me(NO_3)_n{\cdot}qH_2O$ given in Fig. 1 should be completed with the another way leading to nitrous oxide formation. Formally this way could be described by the following reaction:

$$2NO_3^- = N_2O + 2O_2 + O^{2-} \quad (6)$$

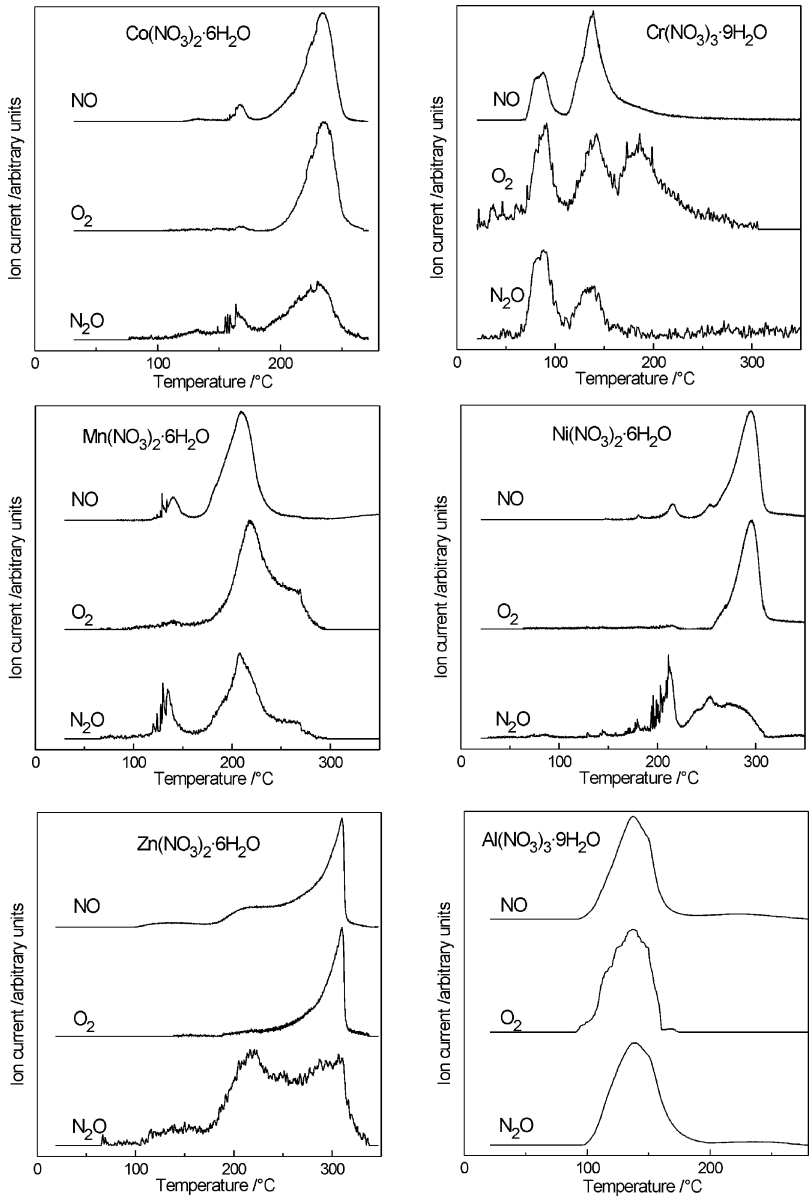

Fig. 2. Ionic currents of NO^+, $O_2{}^+$ and N_2O^+ for decomposition of some metal nitrates as a function of temperature ($\beta = 2\,^{\circ}C\,min^{-1}$, sample mass 12 mg, helium).

However, N_2O in contradiction to NO and NO_2, cannot form during thermal degradation of single $NO_3{}^-$ anion and some kind of synthesis is necessary. This synthesis in N_2O formation is required because of N–N bond existing in nitrous oxide. Two resonance forms of N_2O molecule structure are:

$$\ddot{N}{=}N{=}\ddot{O} \leftrightarrow : N{\equiv}N{-}\ddot{O}:$$

Additionally, the direct reaction given by Eq. (6) is unlikely due to the negative charge of nitrate ions which makes difficult contact between them.

We propose a hypothesis of N_2O formation based on the charge distribution in the dipole formed by NO molecule. Using concept of electronegativity one can expect that electron density in NO molecule is rather higher at oxygen atom because the electronegativity of oxygen is greater than electronegativity of nitrogen. The detailed quantum mechanics calculations show yet that as a result of nitrogen atom hybridization in NO molecule and free electrons pair at N atom ($:\overset{-}{\underset{\cdot\cdot}{N}}=\overset{+}{\underset{\cdot\cdot}{O}}\cdot$) the electron density in NO is higher at nitrogen atom which is negative pole of dipole [10–14]. In the symmetric, flat $NO_3{}^-$ ion (sp^2 hybridization) the negative charge is delocalized between four atoms forming this ion. Due to symmetry, electron density at oxygen atoms have to be the same, and as a result of differences in electronegativity excess of negative charge is observed at these atoms (Fig. 3). That is why in all nitrates $Me^{(+)}{-}^{(-)}O{-}NO_2$ bonds are observed [15]. Theoretical studies of aqueous solutions containing $NO_3{}^-$ ions confirm that negative charge is shifted to oxygen atoms [16]. Thus, the formal charge of nitrogen atom in $NO_3{}^-$ ion in relation to oxygen atoms should be positive [17]. Taking into account the dipole structure of NO and charge distribution in

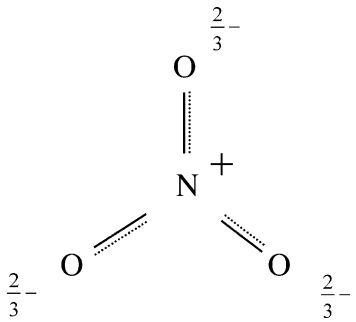

Fig. 3. Hybrid structure of the nitrate ion.

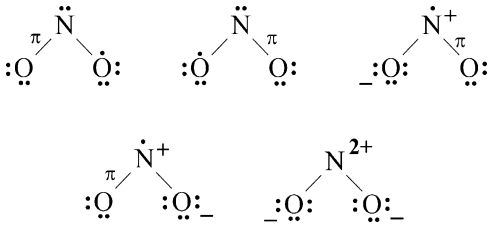

Fig. 4. Resonance structures of NO_2.

the nitrate ion we can point at possibility of reaction given by the following equation:

$$NO + NO_3^- = N_2O + \tfrac{5}{4}O_2 + \tfrac{1}{2}O^{2-} \quad (7)$$

Formation of N–N bond in reaction (7) results directly from interaction between $N^{(-)}$ (NO) and $N^{(+)}$ (NO_3^-).

The nitrogen atom in NO_2 molecule has the valency electrons which do not take part in chemical bonds N–O (Fig. 4). Therefore, the reaction similar to (7) seems to be possible between NO_2 and NO_3^-:

$$NO_2 + NO_3^- = N_2O + \tfrac{7}{4}O_2 + \tfrac{1}{2}O^{2-} \quad (8)$$

The occurrence of the reactions (7) and (8) leads to almost the same type of changes of concentration NO and N_2O in gaseous products of decomposition which is observed in experiments.

The other possibility of N_2O formation during nitrate decomposition is based on the two consecutive reactions:

$$2NO \rightleftarrows N_2O_2 \quad (9a)$$

$$N_2O_2 + NO = N_2O + NO_2 \quad (9b)$$

Reaction (9a) is well documented as occurring in gaseous and liquid phase. The structure of dimer N_2O_2, containing chain of atoms O–N–N–O was described for instance in paper [18]. The second reaction (9b) was mentioned by Melia [19] and to our knowledge it was never reported later. Reactions between N_2O and CO or H_2 which are apparently similar to reaction (9b):

$$N_2O_2 + CO = N_2O + CO_2 \quad (10a)$$

$$N_2O_2 + H_2 = N_2O + H_2O \quad (10b)$$

are described in chemical kinetics handbooks. The carbon monoxide and hydrogen are strong reducing agents contrary to the nitric oxide which has weak reducing properties. This shows that probability of the reaction (9b) is rather low. Additionally oxygen formed during thermal decomposition of nitrates can react with N_2O_2 according to well known reaction:

$$N_2O_2 + O_2 = 2NO_2$$

This decreases the possibility of occurring the reaction (9b).

In result of above considerations mainly the proposed reaction (7) and possible reaction (8) should be considered as sources of N_2O during thermal decomposition of nitrates.

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