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Thermal decomposition of $Cu(NO_3)_2{\cdot}3H_2O$ at reduced pressures

I.V. Morozov[*], K.O. Znamenkov, Yu.M. Korenev, O.A. Shlyakhtin

Inorganic Chemistry Division, Department of Chemistry, Moscow State University, Moscow 119992, Russia

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Abstract

Thermolysis of $Cu(NO_3)_2{\cdot}3H_2O$ is studied by means of XRD analysis in situ and mass spectral analysis of the gas phase at $P = 1/10$ Pa at low heating rate. It is shown that *stage I* of the dehydration (40–80 °C) results in the consecutive appearance of crystalline $Cu(NO_3)_2{\cdot}2.5H_2O$ and $Cu(NO_3){\cdot}H_2O$. Anhydrous $Cu(NO_3)_2$ formed during further dehydration at 80–110 °C is moderately sublimed at 120–150 °C. Dehydration is accompanied by thermohydrolysis, leading to the appearance of $Cu_2(OH)_3NO_3$ and gaseous H_2O, HNO_3, NO_2, and H_2O. The higher pressure in the system, the larger amount of thermohydrolysis products is observed. The formation of the crystalline intermediate $CuO_x(NO_3)_y$ was observed by diffraction methods. Final product of thermolysis (CuO) is formed at 200–250 °C.

Keywords: Copper nitrate; Thermal decomposition; Evolved gas analysis; Mass spectrometry

1. Introduction

$Cu(NO_3)_2{\cdot}3H_2O$ is one of the most popular precursor components, used in the preparation of various materials including high-temperature superconductors. The character of its thermal decomposition depends greatly on the processing conditions, first of all on the total pressure in the system. The most of investigators [1–5] observed two or three stages of $Cu(NO_3)_2{\cdot}3H_2O$ thermolysis at atmospheric pressure: melting of hydrate at 116–152 °C; formation of β-$Cu_2(OH)_3NO_3$ (199–217 °C) and its decomposition to CuO (263–310 °C). Formation of the oxynitrate $Cu_7O_{8-x}NO_3$ was observed during thermolysis of $Cu(NO_3)_2{\cdot}3H_2O$ in oxygen [6].

Thermal decomposition of $Cu(NO_3)_2{\cdot}3H_2O$ at reduced pressures [7–11] occurs in the solid state. After the primary dehydration simultaneous release of water and nitrogen-containing species (NO, NO_2) was observed. The last process is accompanied by the formation of $Cu_2(OH)_3NO_3$ at 167–205 °C [9] or $3Cu(NO_3)_2{\cdot}Cu(OH)_2$ (65–107 °C) [7]. The final product of decomposition is CuO ($T = 182$–312 °C [7], 247–260 °C [9]).

Anhydrous $Cu(NO_3)_2$ was not observed among solid intermediates, though several groups reported the appearance of $Cu(NO_3)_2$ molecules in the gas phase. To explain this phenomenon, along with sublimation [7], the mechanism of trapping of gaseous thermolysis products by solid state particles because of “crystal rearrangement” have been proposed [10]. Authors in [9] consider the appearance of Cu-containing ions in the mass spectrum of decomposition products as an evidence of total evaporation of precursor substance followed by its decomposition and solidification of products.

In order to explain anomalously low amount of oxygen among gaseous products of decomposition, the formation of gaseous HNO_3 is proposed [7].

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[*] Corresponding author. Fax: +7-95-939-09-98.
E-mail address: morozov@inorg.chem.msu.ru (I.V. Morozov).

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Conversely, appearance of O_2^+ signal at the last stage of decomposition is ascribed to catalytic decomposition of NO_2 on the surface of CuO particles [9].

Most of the mentioned conclusions concerning amount and composition of the intermediate products of thermolysis at reduced pressures are based on the results of the dynamic mass spectrometry of the gas phase confirmed in some instances by thermogravimetric investigations [7,11]. Specific feature of our approach is combination of mass spectral analysis with careful XRD study of solid intermediates. Following experiments and considerations allowed us to propose self-consistent scheme of thermal decomposition of $Cu(NO_3)_2{\cdot}3H_2O$, based on the existence of two different thermolysis ways at normal pressure and in vacuum.

2. Experimental

Mass spectral investigation of gaseous products of thermal decomposition was realized by means of MX-1303 mass spectrometer with magnetic mass analyzer and electron impact ionization; gas inlet system was adapted to high-temperature thermodynamic studies. General conditions of MS experiments were as follows: $U_{ion} = 70\,V$, $U_{acc} = 3.00\,kV$, $I_{emis} = 0.9\,\mu A$. Basic features of device design and experimental methods can be found in [12].

During decomposition experiments, platinum Knudsen cell was loaded with 110 mg of $Cu(NO_3)_2{\cdot}2.5H_2O$ and heated up at 1–4 $K\,h^{-1}$ with intermediate isothermal steps (Fig. 1A) in order to ensure equilibrium composition of the gaseous products, monitored by intensity control of several peaks, corresponding to various H-, N-, O- and Cu-containing species. Attribution of peaks to various products has been made using reference spectra of H_2O, O_2, NO, NO_2 [13].

Phase composition of solid intermediates has been studied by separate experiments. Four ampoules with $Cu(NO_3)_2{\cdot}2.5H_2O$ were heated up simultaneously at heating rate 10 $K\,h^{-1}$ in dynamic vacuum ($P = 1$ Pa). When the temperatures 80, 100, 140 and 170 °C were achieved, corresponding ampoules were quenched and sealed off for further XRD study. XRD analysis has been performed using DRON-4 diffractometer at Cu Kα radiation; hygroscopic samples of intermediate products have been processed in dry box and protected by polystyrene film during measurement. Analysis of Cu content and oxidation degree was realized by comparative iodometric titration. The transformation in the solid state has been also studied by in situ XRD using high-temperature vacuum attachment to the Guinier-de Wolf diffraction camera (Cu Kα, $P =$ 1 Pa, heating rate 1 $K\,min^{-1}$; Ge as internal standard).

3. Results and discussion

Analysis of the gaseous products of thermal decomposition of nitrates is complicated by appearance of identical fragments during ionization of various NO_x-containing species. Main method of the product identification in this case is based on the various ionic currents intensity ratio of several basic fragments (NO^+, NO_2^+, O_2^+) for various NO_x products. Using this attribution method, it is clearly seen that at $T <$ 190 °C the ratio of ionic currents $I(NO^+)/I(NO_2^+)$ is essentially less than value of 2.70 for NO_2 molecules [13] usually considered as the main gaseous decomposition product at these temperatures. This difference points to the presence of nitrogen-containing molecules with a higher oxidation degree of nitrogen; most probable of them is HNO_3. To obtain reference mass spectrum of nitric acid, HNO_3 has been produced in situ, in Knudsen cell, by reaction of thermal decomposition of cesium hydronitrate, prepared according to [14]:

$$Cs[H(NO_3)_2]_{(cr)} = CsNO_{3(cr)} + HNO_{3(g)} \qquad (1)$$

Experimentally observed value of $I(NO^+)/I(NO_2^+)$ for as-obtained HNO_3 vapors was 0.25.

Using as-obtained mass spectrum of HNO_3 and reference spectra of another molecules [13], qualitative and quantitative analysis of gas phase composition can be performed. According to this consideration, H_2O, HNO_3, NO_2 and O_2 are the principal constituents of the gas phase throughout almost the whole decomposition process. It should be noted also that at the final stage of decomposition ($T = 192$–222 °C) mean ratio of $I((NO^+)/I(NO_2^+) = 2.4$, i.e. it is rather close to the data for reference spectrum of NO_2 [13].

Experimental observation of mass spectral lines, corresponding to $Cu(NO_3)_2^+$, $Cu(NO_3)^+$, CuO^+ and Cu^+ with characteristic ratio between their intensities, shows at the appearance of $Cu(NO_3)_2$ molecules

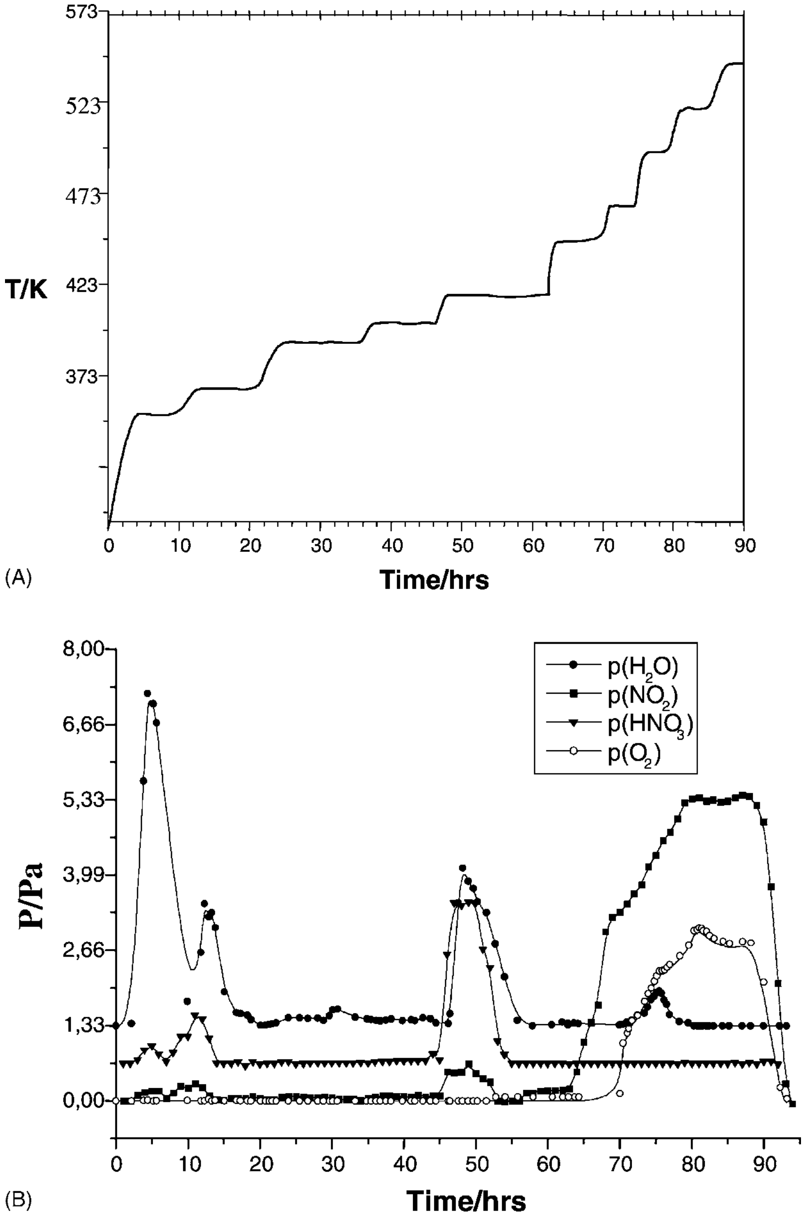

Fig. 1. Vacuum decomposition of $Cu(NO_3)_2 \cdot 2.5H_2O$ in the Knudsen cell: (A) temperature vs. time plot; (B) evolved gas analysis plots for the main gaseous products of thermolysis.

in the gas phase. This fact corresponds quite well to the data of works [15,16]; no other Cu-containing molecules or fragments were found in the gas phase. Similar process, observed in [17] during decomposition of $Cu(NH_3)_4(NO_3)_2$, shows at the outstanding stability of free $Cu(NO_3)_2$ molecules. The experiment was finished at $T = 270\,^{\circ}C$, when the gas release from Knudsen cell was over. Mass losses due to effusion of $Cu(NO_3)_2$ appeared to be less than 1.5%.

Using obtained experimental data, ionic currents j from molecules i (I_{ij}) were recalculated into corresponding partial pressures P_i of gaseous products of reaction, released from Knudsen cell during thermolysis. The following equation was used [18]:

$$P_i = \frac{k}{\sigma_i} I_i T \qquad (2)$$

where P_i is the partial pressure of molecules i, k the sensitivity factor of the mass spectrometer, σ_i the total ionization cross section of a molecule i, $I_i = \Sigma I_{ij}$ the total ion current produced upon ionization of molecules i, T the temperature. The values of σ_i have been calculated by an additive scheme using σ values for atoms from [18].

Presentation of as-obtained partial pressure values for different decomposition products as a function of processing time (Fig. 1B), and, hence, processing temperature (Fig. 1A) and comparison of these data with results of XRD analysis of intermediates allows to conclude that thermal decomposition of $Cu(NO_3)_2{\cdot}3H_2O$ in vacuum differs significantly from the corresponding process at atmospheric pressure described in the literature. Observed decomposition process can be divided into three distinct stages of various physico-chemical nature.

Stage I (40–80 °C) consists of the stepwise dehydration of $Cu(NO_3)_2{\cdot}3H_2O$:

$$Cu(NO_3)_2 \cdot 3H_2O_{(cr)} = Cu(NO_3)_3 \cdot 2.5H_2O_{(cr)} + 0.5H_2O_{(g)} \qquad (3)$$

$$Cu(NO_3)_2 \cdot 2.5H_2O_{(cr)} = Cu(NO_3)_2 \cdot H_2O_{(cr)} + 1.5H_2O_{(g)} \qquad (4)$$

Quantitative transformation of trihydrate into $Cu(NO_3)_2{\cdot}2.5H_2O$ proceeds at $T \geq 45\,^{\circ}C$. According to the literature data, the amount of H_2O in commercially available hydrates usually exceeds by 0.5 molecule the corresponding value, determined by means of monocrystal X-ray diffraction method $(Cu(NO_3)_2(H_2O)_2{\cdot}0.5H_2O)$. Apart from $Cu(NO_3)_2{\cdot}3H_2O$, crystallized from usual aqueous solutions, $Cu(NO_3)_2{\cdot}2.5H_2O$ can be obtained by slow crystallization from acid solutions of copper nitrate. X-ray crystal structure analysis, performed in [19], demonstrated complete identity of both hydrates. The dehydration can be stopped at this step, while further dehydration is accompanied by the formation of recently discovered monohydrate [20,21]. The dehydration is accompanied by significant thermohydrolysis (5); released HNO_3 is partially dissociated according to Eq. (6).

$$2Cu(NO_3)_2 \cdot 2.5H_2O_{(cr)} = Cu_2(OH)_3NO_{3(cr)} + 2H_2O_{(g)} + 3HNO_{3(g)} \qquad (5)$$

$$2HNO_{3(g)} = 2NO_{2(g)} + H_2O_{(g)} + \tfrac{1}{2}O_{2(g)} \qquad (6)$$

Further dehydration of $Cu(NO_3)_2{\cdot}H_2O$ at 80–100 °C results in the formation of the mixture of two polymorphs of anhydrous copper(II) nitrate:

$$Cu(NO_3)_2 \cdot H_2O_{(cr)} = Cu(NO_3)_{2(cr)} + H_2O_{(g)} \qquad (7)$$

In compliance with [22], significant amount of amorphous modification of hydroxonitrate is also formed along with α-$Cu_2(OH)_3NO_3$. So, *stage II* can lead to the formation of four solid intermediates: α- and β-$Cu(NO_3)_2$, α-$Cu_2(OH)_3NO_3$ and amorphous copper hydroxonitrate.

Stage II of thermolysis (100–150 °C) deals with thermal decomposition of hydroxonitrate and sublimation of anhydrous $Cu(NO_3)_2$. According to [22], at 135–140 °C amorphous $Cu_2(OH)_3NO_3$ crystallizes into α-modification, which transforms into β-polymorph at 140–150 °C. Intensive evolution of H_2O, NO_2 and HNO_3 to the gas phase at $T = 143\,^{\circ}C$ (Fig. 1B) shows at the decomposition of hydroxonitrate, accompanied by partial breakdown of HNO_3 (see reaction (6)):

$$Cu_2(OH)_3NO_{3(cr)} \rightarrow 2CuO_{(cr)} + HNO_{3(g)} + H_2O_{(g)} \qquad (8)$$

Observed temperature of thermal decomposition of $Cu_2(OH)_3NO_{3(cr)}$ is found to be less than in [23] (160–235 °C) because of the lower pressure and heating rate, applied in the present work.

Abundance of HNO_3 in the gas phase through the most part of decomposition process explains the absence of substantial ionic current of $O_2{}^+$ in the mass spectrum. It should be marked also that appearance of HNO_3 in the gas phase is confirmed at the present work by close coincidence of experimental and theoretical mass spectra.

Compared to initial substance, the residue after sublimation is enriched by β-polymorph of $Cu(NO_3)_2$, which corresponds quite well to the data of [21]. The polymorph transition of $Cu(NO_3)_2$ can be also realized quantitatively in the sealed quartz ampoule for 24 h at 140 °C:

$$\alpha\text{-Cu(NO}_3)_{2(\text{cr})} \rightarrow \beta\text{-Cu(NO}_3)_{2(\text{cr})} \qquad (9)$$

Cautious thermolysis of $Cu(NO_3)_2{\cdot}3H_2O$ at reduced pressures can be used for the synthesis of anhydrous $Cu(NO_3)_2$. Thermal treatment of 0.5 g of $Cu(NO_3)_2{\cdot}3H_2O$ at $P = 2$–4 Pa at 80–95 °C for 2 h followed by heating to 150 °C for 3 h resulted in the preparation of $Cu(NO_3)_2$ condensate with the yield of 10–15%. At the same time substitution of $Cu(NO_3)_2{\cdot}3H_2O$ with separately prepared according to [21] $Cu(NO_3)_2{\cdot}H_2O$ as precursor enhances the yield of sublimation up to 70%. The yield is decreased with increasing pressure and heating rate. This fact shows at the strong competition between dehydration itself and thermohydrolysis processes during thermal decomposition; all factors increasing the partial pressure of water vapors promote thermohydrolysis while amount of anhydrous and volatile $Cu(NO_3)_2$ decreases simultaneously.

Detection of $Cu(NO_3)_2$ by non-diffraction methods is also complicated by its simultaneous appearance with $Cu_2(OH)_3(NO_3)$. Formation of similar mixture can be responsible for unusual composition of intermediate phases, reported in several papers (for example, $3Cu(NO_3)_2{\cdot}Cu(OH)_2$ in [7]), when thermogravimetric method was applied for identification of intermediates.

In the last, *stage III* of the process (180–220 °C) the character of the mass spectrum is drastically changed: ionic current $I(H_2O^+)$ drops to almost background level, the ratio $I(NO_2{}^+)/I(NO^+)$ fits well to the mass spectrum of NO_2, ionic currents of Cu-containing species are disappeared along with appearance of unusually high ionic current of O_2. The gap between NO_2 and O_2 release curves at this stage (Fig. 1B) shows at the probable formation of intermediate oxonitrate, which can contain Cu^{3+}:

$$Cu(NO_3)_{2(\text{cr})} \rightarrow CuO_x(NO_3)_{y(\text{cr})} + NO_{2(\text{g})} + O_{2(\text{g})} \qquad (10)$$

Similar process can occur also at *stage II* during decomposition of $Cu_2(OH)_3NO_3$. This idea was confirmed by the data of in situ X-ray diffraction experiment (Fig. 2): appearance of the CuO diffraction patterns at the upper part of the chart is preceded at 170–200 °C by emergence of several lines (marked as “x” at Fig. 2), which cannot be attributed neither to known copper nitrates nor hydroxonitrates or oxynitrate $Cu_7O_{8-x}NO_3$.

In order to confirm the existence of this phase, several experiments have been performed. The samples of $Cu(NO_3)_2{\cdot}3H_2O$ were heated in dynamic vacuum (1–6 Pa) from 20 to 170–190 °C using various heating rates and masses of samples. XRD patterns of almost all samples, along with strong lines of $Cu_2(OH)_3NO_3$, contained several new lines, belonging to the “X-phase”: d = 7.82 Å (100%), 6.26 Å (20%), 5.23 Å (20%), 3.43 Å (50%), 3.28 Å (20%).

Then the final part of the decomposition processes, occurred at the *stage III* of thermolysis, can be described as follows:

$$\begin{aligned}&CuO_x(NO_3)_{y(\text{cr})}\\ &\quad\rightarrow CuO_{(\text{cr})} + yNO_{2(\text{g})} + \tfrac{1}{2}(x + y - 1)O_{2(\text{g})}\end{aligned} \qquad (11)$$

In [9], ionic current of $O_2{}^+$ was also detected only at the last stage of the thermal decomposition of $Cu(NO_3)_2{\cdot}3H_2O$, though this fact has been attributed to the catalytic action of copper(II) oxide on the dissociation of NO_2. In authors’ [9] opinion, the solid product of decomposition in this process is $Cu_2(OH)_3NO_3$. Probably, as applied decomposition rate was rather high (60 K min^{-1}), the stages of $Cu_2(OH)_3NO_3$ and $CuO_x(NO_3)_y$ decomposition were coincided.

Finally, we can conclude that thermal treatment of copper(II) nitrate trihydrate in vacuum is accompanied by drastic competition of dehydration and thermohydrolysis processes, which can be schematically presented at Fig. 3. The contribution of dehydration processes is increased as the pressure in the system is decreased. The basic dissimilarity of vacuum dehydration from the similar process at atmospheric pressure is not only lower temperature of realization, but also another mechanism of the process. Main feature of this mechanism is formation of crystalline $Cu(NO_3)_2{\cdot}H_2O$ and, then, $Cu(NO_3)_2$, which have not been observed by previous authors. Another peculiarity of vacuum dehydration is formation of HNO_3 vaporous as one of the main gaseous products of thermolysis. Further thermal decomposition of $Cu(NO_3)_2$ is accompanied by the formation of crystalline copper oxynitrate which is considerably different from $Cu_7O_8NO_3$, described in [6], both by structural features and lower thermal stability.

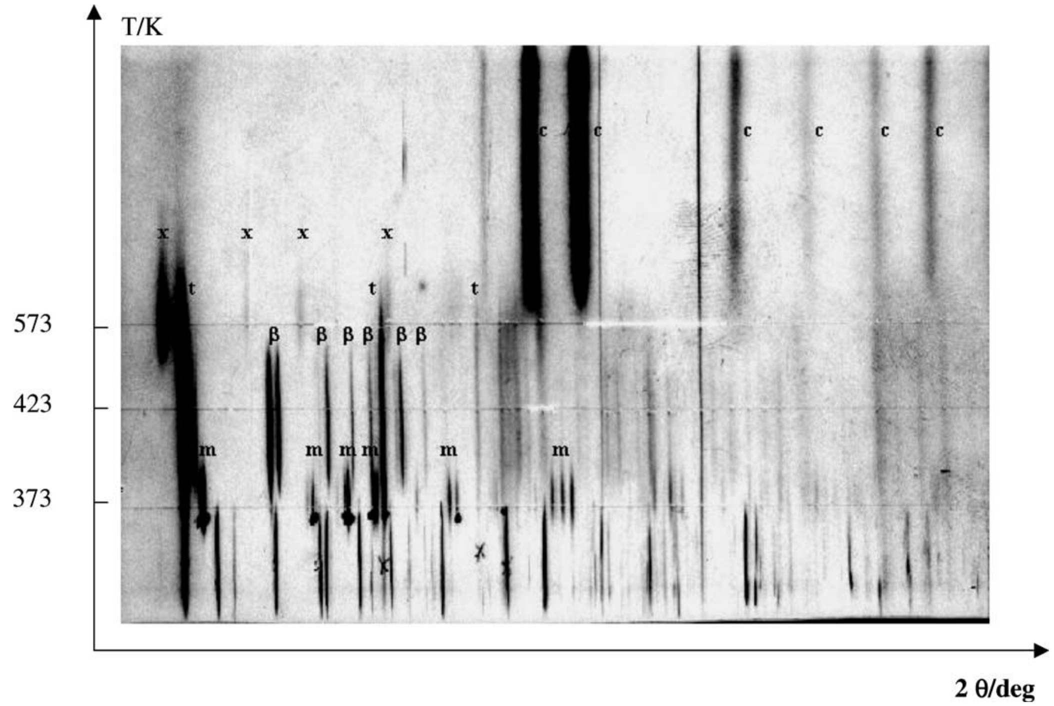

Fig. 2. High-temperature XRD diffraction pattern of $Cu(NO_3)_2 \cdot 2.5H_2O$ during vacuum dehydration: (m) $Cu(NO_3)_2 \cdot H_2O$; (t) $Cu_2(OH)_3NO_3$, (β) β-$Cu(NO_3)_2$, (x) unidentified oxynitrate CuO_xNO_3 (“X-phase”); (c) CuO.

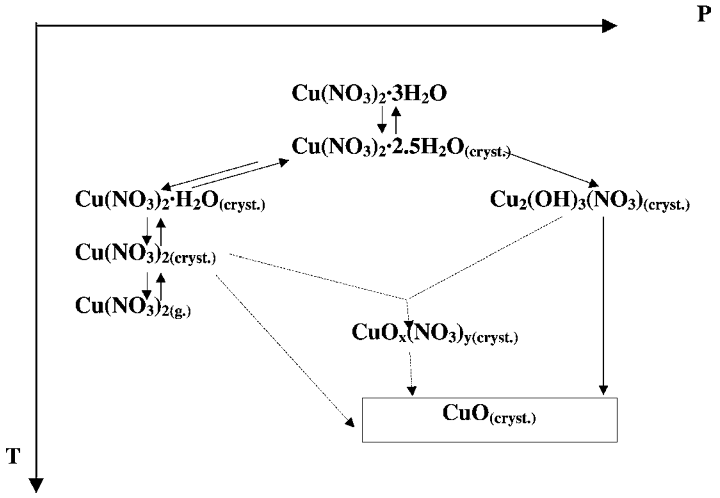

Fig. 3. Scheme of the thermal decomposition of $Cu(NO_3)_2 \cdot 2.5$ H_2O at atmospheric pressures. Solid and dashed lines indicate proven and assumed processes respectively.

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References

[1] S. Gordon, C. Campbell, Anal. Chem. 27 (1955) 1102.
[2] T. Cseri, S. Bekassy, G. Kenessey, G. Liptay, F. Figueras, Thermochim. Acta 288 (1966) 137.
[3] A.M. Sirina, I.I. Kalinichenko, A.I. Purtov, Russ. J. Inorg. Chem. (Int. Ed.) 15 (9) (1970) 1258.
[4] J. Ghose, A. Kanungo, J. Therm. Anal. 20 (1981) 459.
[5] J. Mu, D.D. Perlmutter, Thermochim. Acta 49 (1981) 207.
[6] I. Yarawa, R. Sugise, N. Terada, M. Jo Kunihikooka, H. Hayakawa, I. Hideo, Jpn. J. Appl. Phys. 29 (8) (1990) 1480.
[7] D. Dollimore, G.A. Gamlen, T.G. Taylor, Thermochim. Acta 103 (1986) 333.
[8] P. Wang, V. Majidi, J.A. Holcombe, Anal. Chem. 61 (1989) 2652.
[9] B.V. L'vov, A.V. Novichikhin, Spectrochim. Acta B 50 (1995) 1459.
[10] J.G. Jackson, R.W. Fonseca, J.A. Holcombe, Spectrochim. Acta B 50 (1995) 1449.
[11] D. Weigel, B. Imelik, M. Prettre, Bull. Soc. Chim. Fr. 4 (1964) 836.
[12] Y.M. Korenev, A.N. Rykov, S.V. Kuznetsov, A.I. Boltalin, A.V. Novoselova, Russ. J. Inorg. Chem. 31 (7) (1986) 1832.
[13] I.L. Agafonov, G.G. Devyatykh. Mass Spectrometry of Gases and Vapors of High Purity, Nauka, Moscow, 1980.
[14] M.A. Yakimov, V.Y. Mishin, Russ. J. Inorg. Chem. 8 (1963) 227.
[15] S.C. Wallwork, Proc. Chem. Soc. (Lond.) 1 (1959) 11.
[16] C.C. Addison, B.J. Hathaway, Advances in Mass Spectrometry, vol 5, Pergamon Press, New York, 1971, p. 379.
[17] S.S. Dyukarev, I.V. Morozov, et al., Rus. J. Inorg. Chem. 44 (6) (1999) 945–950.
[18] L.N. Sidorov, M.V. Korobov, L.V. Zhuravleva, Mass-spectral thermodynamic studies, Moscow, MSU, 1985.
[19] J. Garaj, Acta Chem. Scand. 22 (1968) 1710.
[20] S.I. Troyanov, I.V. Morozov, K.O. Znamenkov, Yu.M. Korenev, V.V. Ichenko, O.A. Shlyakhtin, Kurzreferate der Konferenz, Festkoperchemie als Grundlage der Materialforshung, Bonn, 1994, p. 174.
[21] S.I. Trojanov, I.V. Morozov, K.O. Znamenkov, Y.M. Korenev, Z. Anorg. Allg. Chem. 621 (1995) 1261.
[22] Z. Oswald, Z. Kristallogr, Kristallgeom. Kristallphys. Kristallchem. 116 (1961) 210.
[23] I. Schildermans, J. Mullens, et al., Thermochim. Acta 224 (1993) 227.