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Mechanism of thermal decomposition of cadmium nitrate $Cd(NO_3)_2 \cdot 4H_2O$

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Abstract

The thermal decomposition of $Cd(NO_3)_2 \cdot 4H_2O$ was studied using DTA, TG, QMS and XRD techniques. It has been found that decomposition process of this compound proceeds through three stages. A possible mechanism for the investigated process has been proposed. The quasi-isothermal method was used to determine the activation energy E_{act} values of thermal decomposition of $Cd(NO_3)_2$. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Cadmium nitrate; Thermal decomposition; Thermal analysis; Kinetics

1. Introduction

Metal nitrates are widely used as precursors in the production of metal oxides for high surface catalysts, molecular sieves, ceramics and electronic materials (e.g. semiconductors, gas sensors). Little appears though to be known about the processes occurring when nitrates are converted thermally to the oxides and the thermal decomposition of transition metal nitrates has been a little studied field. Most transition metal nitrates are hydrated and so do not decompose in simple stages [1–5]. In the case of cadmium nitrate it is possible to obtain the anhydrous salt by drying but its mechanism of thermal decomposition is also not quite clear.

Duval [6] has found that the decomposition of $Cd(NO_3)_2 \cdot 4H_2O$ proceeds via dehydration in two steps to anhydrous cadmium nitrate which undergoes further decomposition to CdO in one step. Nikolova and Maneva [7] have found evidence of melting of the initial hydrates and deuterates followed by single-stage dehydration of the melt to yield the anhydrous salt. T_m, $\Delta H^0_m, \Delta S^0_m$ values were determined for the hydrates studied. Bérnard et al. [8] determined the crystal structure of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and its mechanism of decomposition. They observed that under vacuum $Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O$ was obtained during the first stage, whereas an anhydrous form of hydroxide nitrate $Cd(OH)(NO_3)$ was yielded in the second stage.

During the investigations of decomposition mechanisms of $Cd(NO_3)_2 \cdot 4H_2O$, the appearance of metal oxides in the gas phase at low temperatures has been observed. The unusual appearance of metal oxides and nitrates, well below the temperatures at which they exhibit a measurable vapour pressure, has raised the question regarding their origin. L'vov and Novichikhin [9] have proposed a ''gasification'' process whereby the decomposition of metal nitrates proceeds through the gaseous metal oxide as an inter-

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mediate product:

$$MNO_{3(s)} \rightarrow MO_{(g)} + 2NO_2 + 0.5O_2 \qquad (1)$$

followed by

$$MO_{(g)} \rightarrow MO_{(s)} \qquad (2)$$

In their opinion the whole decomposition process of the $Cd(NO_3)_2$ occurs via the gaseous phase. Jackson et al. [10,11] disagreed with this conclusion and assumed a decomposition mechanism in the solid state. They have suggested that the explanation of appearance of the cadmium oxide in gaseous phase is "crystal shattering", occurring as a result of rearrangement during the decomposition of the nitrate to the oxide.

In view of the available data, the decomposition mechanism of $Cd(NO_3)_2$ requires additional investigation. In our paper we have tried to clarify problems concerning the process of decomposition of this compound.

2. Experimental

2.1. Material

The $Cd(NO_3)_2{\cdot}4H_2O$ used was "pure for analysis" grade (POCh, Gliwice, Poland). The content of the water of crystallisation was confirmed by mass analysis. The sample was used without additional preparation procedure.

2.2. SDT analysis

The TG and DTA curves were recorded with a SDT 2960 TA Instruments apparatus. The samples were heated in standard platinum crucibles at a rate 0.5–20 K min^{-1} in helium or air flowing at a rate of 100 cm^3 h^{-1}. The average masses of the samples were 10 mg. Simultaneously, evolved gas analysis (EGA) was performed with a quadruple mass spectrometer (QMS), model ThermoStar Balzers Instruments. The spectrometer was connected to the outlet of the SDT apparatus with heated quartz capillary. The QMS was operated with an electron impact ionizer with electron energy 70 eV. The spectra lines were monitored for *m/z* values equal: 12, 14, 16, 17, 18, 28, 30, 32, 44, 46 and 63. All data collection was performed by an on-line connected computer system with commercial (TA Instruments, Balzers Instruments) software.

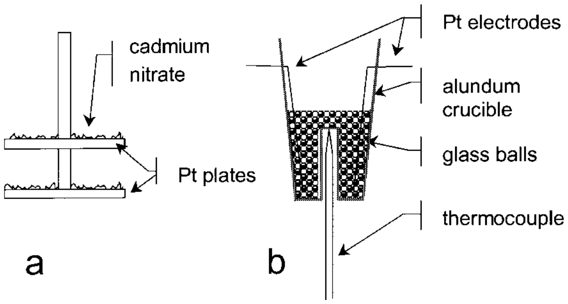

Fig. 1. Plate-shape crucible (a) and ceramic crucible for electric conductivity measurements (b).

The experiments with controlled rate of decomposition (so-called quasi-isothermal conditions) were performed by means of an electronic thermobalance with computer-based data processing system. The controlled rates of decomposition were 0.2–10 mg min^{-1}. The initial masses of the samples were 650–750 mg. The samples were placed on the plate-shape, platinum crucibles (Fig. 1 (a)) to achieve good conditions for carrying away gaseous products of the reaction. The decomposition processes were performed in a dynamic (15 dm^3 h^{-1}) atmosphere of air. The thermobalance was also used for the preparation of solid products of partial decomposition for XRD analysis.

The conductivity measurements were carried out simultaneously with DTA and TG analysis for precise determination of the melting and solidification temperatures. The sample was placed in the ceramic crucible with two fixed platinum electrodes (Fig. 1 (b)). The crucible was filled with glass balls (ϕ=0.7 mm) to prevent formation of gas bubbles in the molten cadmium nitrate. The measurements were performed with an AC conductometer with frequency 1 kHz.

3. Results and discussion

The TG, DTA and selected QMS curves recorded for $Cd(NO_3)_2{\cdot}4H_2O$ at 2.5 K min^{-1} in a dynamic atmosphere of helium are shown in Fig. 2. The figure indicates that decomposition proceeds in three stages. In the first stage (T=320–350 K) $Cd(NO_3)_2{\cdot}4H_2O$ melts (T_{m_1}=327 K) and undergoes dehydration to the approximate composition $Cd(NO_3)_2{\cdot}2H_2O$. The DTA peak is a result of two endothermic effects –

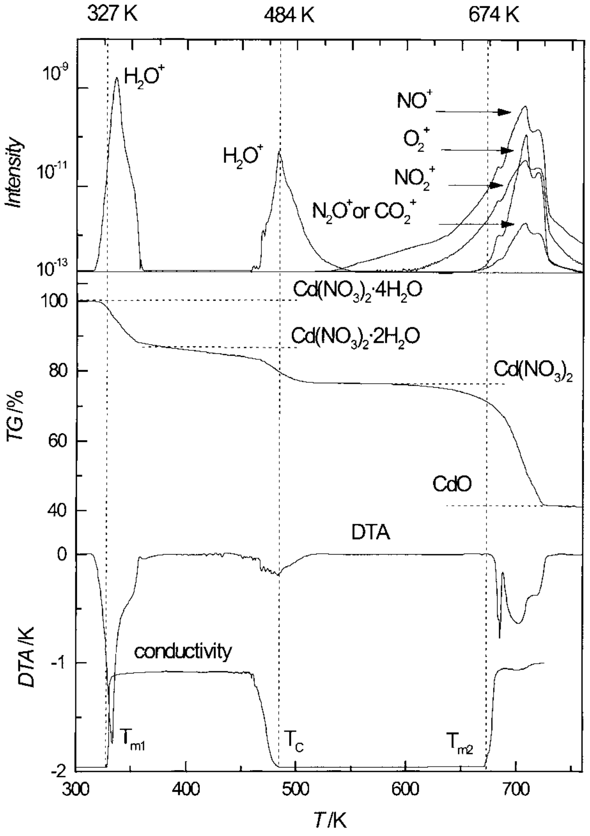

Fig. 2. DTA, TG, EGA and conductivity curves for the thermal decomposition of $Cd(NO_3)_2 \cdot 4H_2O$ in helium (heating rate: 2.5 K min^{-1}).

melting and dehydration. In the second stage the melt loses the remaining water and solid anhydrous cadmium nitrate is formed. The corresponding DTA peak is smaller than the first one due to the superposition of the endothermic dehydration and the exothermic crystallisation. These results differ significantly from results presented in [7] where the authors observed only melting at 331 K and single-stage dehydration at 466 K. This difference may be the effect of higher rate of heating (5 K min^{-1}) or different sample size.

The decomposition of $Cd(NO_3)_2$ proceeds probably in one stage with melting at T_{m_2}=674 K. Although the DTA peak and related QMS peaks have complex shapes, the XRD analysis of the partial products of decomposition (obtained for TG=70%, 60%, 50% and 45%) showed that the solid/liquid products are only a mixture of the $Cd(NO_3)_2$ and the final product – CdO. No other intermediate products were noticed. This observation is fully consistent with TRXD results described elsewhere [8]. The complex shape of the DTA and QMS peaks can be explained by the physical changes in the sample during the solidification process.

The QMS spectra display the presence of O_2, NO, NO_2 in the gaseous products in the last step of the decomposition process. Ionisation of the NO_2 molecules by 70 eV electrons produces fragmentation of NO_2 to NO. The calculated intensity ratio $NO^+/NO_2^+ = 2.7$ at peak maximum corresponds to the reported value of 2.7 [12]. This indicates that during the decomposition NO_2 is produced as the main product. This observation is fully consistent with the following mechanism proposed for other anhydrous nitrates of divalent metals [13]:

$$Cd(NO_3)_2 \Rightarrow CdO + 2NO_2 + 0.5O_2 \qquad (3)$$

In the QMS spectra a weak signal for m/z=44 is also observed. It corresponds to N_2O or CO_2. The presence of a small parallel peak for m/z=12 (C^+) may suggest that it comes from CO_2. It means that preparation used in our study might contain a small amount of $CdCO_3$. The presence of non-volatile species – Cd, CdO, $Cd(NO_3)^+$, which were observed by L'vov and Novichikhin [9] and Jackson et al. [10,11], could not be monitored due to construction of our apparatus (a long capillary connecting the mass spectrometer and SDT apparatus). However, the observed mass loss of the samples was in a very good agreement (with an accuracy of 0.1%) with the stoichiometry of the proposed reaction (3). This indicates that under our conditions (atmospheric pressure) the evaporation of non-volatile species is negligible. On the other hand, some nitrates of Cu [14], K, Rb, Cs [15] and other cadmium salts (e.g. $CdCl_2$ [16]) are volatile and undergo sublimation or evaporation. It is possible that the appearance of metal oxides and nitrates reported in [9–11] can be the result of sublimation/evaporation of cadmium nitrate in high vacuum.

4. Kinetics

Fig. 2 shows that the thermal decomposition of the $Cd(NO_3)_2$ can proceed in the solid or the liquid

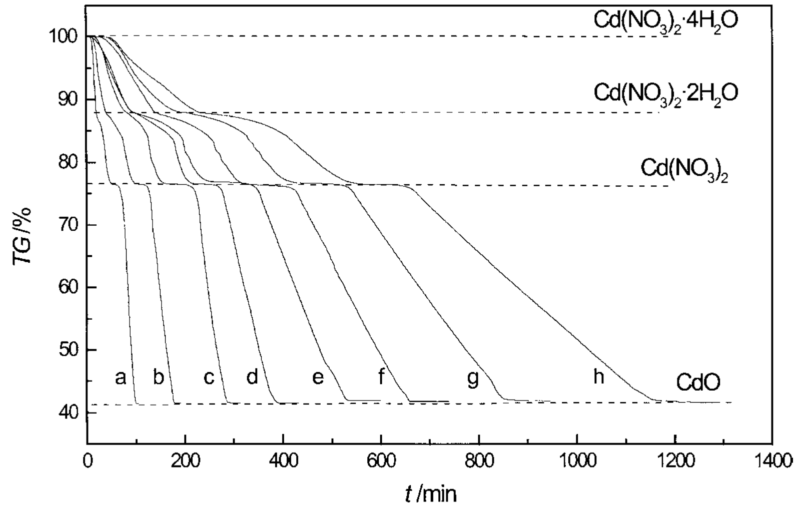

Fig. 3. Kinetic curves for the thermal decomposition of $Cd(NO_3)_2{\cdot}4H_2O$ under quasi-isothermal conditions in air (decomposition rates: (a) 10; (b) 5; (c) 3.5; (d) 2; (e) 1.5; (f) 1; (g) 0.75; and (h) 0.5 mg min^{-1}).

phase depending on conditions of the experiment. The application of the measurements with controlled rate of decomposition (so-called quasi-isothermal conditions) allows the process to be investigated in the liquid or the solid state. Quasi-isothermal measurements can also be used to determinate the activation energy E_{act}. The experimental values of the activation energies were determined by constructing plots for linear form of Arrhenius equation

$$\ln V_d = \frac{-E_{act}}{RT_{TG}} + \text{const.}, \tag{4}$$

where V_d is the controlled rate of decomposition and T_{TG} – the temperature at mass loss TG.

As an example, Fig. 3 shows kinetic curves obtained for various established rates of decomposition and Fig. 4 presents Arrhenius plot received for TG=65%. The estimated value of E_{act}=186±11 kJ mol^{-1} is comparable with reported values of 177 and 188 kJ mol^{-1} [10].

L'vov and Novichikhin [9] assumed in their theory that all reaction products, irrespective of their saturated vapour pressure, transfer initially to the gas phase. The rate of the process is governed by the equilibrium partial pressure of the gaseous products. On the basis of this assumption they have obtained the following relationship between activation energy E_{act} and enthalpy H_T:

$$E_{act} = \Delta H_T/\nu, \tag{5}$$

where ΔH_T is the enthalpy of the evaporation process and ν the sum of the coefficients of the reaction products (the reaction order).

The plot in Fig. 4 indicates that the activation energies for the decomposition of the liquid and the

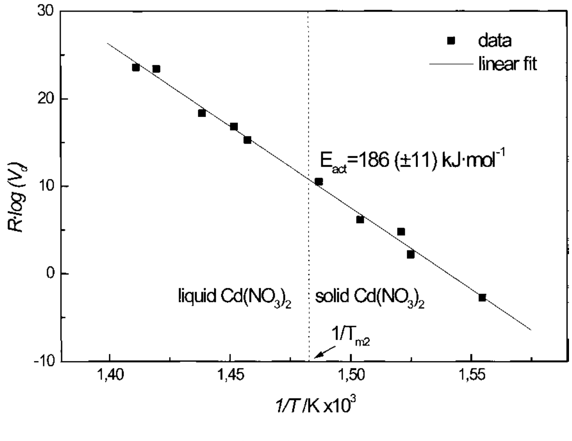

Fig. 4. Arrhenius plot for the thermal decomposition of $Cd(NO_3)_2{\cdot}4H_2O$ in the liquid and the solid state.

solid salt have the same value. This was confirmed by a parametric statistical test of differences between slopes of the regression lines for the signification level α=0.05. This result contradicts the mechanism for metal nitrate decomposition proposed by L'vov and Novichikhin [9] because, according to Hess's law, evaporation enthalpies for the solid and the liquid state should be different.

5. Conclusions

Our results demonstrate that the decomposition of the $Cd(NO_3)_2{\cdot}4H_2O$ proceeds in three stages:

$$Cd(NO_3)_2 \cdot 4H_2O_{(s/l)} \rightarrow Cd(NO_3)_2 \cdot 2H_2O_{(s/l)} + 2H_2O_{(g)} \tag{6}$$

$$Cd(NO_3)_2 \cdot 2H_2O_{(s/l)} \rightarrow Cd(NO_3)_{2(s/l)} + 2H_2O_{(g)} \tag{7}$$

$$Cd(NO_3)_{2(s/l)} \rightarrow CdO_{(s)} + 2NO_{2(g)} + 0.5O_{2(g)} \tag{8}$$

The activation energy values calculated for thermal decomposition of liquid and solid $Cd(NO_3)_2$ suggest that the thermal decomposition of this salt cannot occur according to "gasification" theory proposed by L'vov and Novichikhin [9]. The mechanism involving direct production of CdO through recrystallisation in the solid or the liquid phase seems to be more probable.

Acknowledgements

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References

[1] A. Małecki, S. Łabuś, R. Gajerski, B. Prochowska-Klisch, J. Therm. Anal. (1998), special issue, in press.
[2] A. Małecki, R. Gajerski, S. Łabuś, B. Prochowska-Klisch, K. Wojciechowski, J. Therm. Anal. 39 (1993) 545.
[3] A. Małecki, A. Małecka, R. Gajerski, B. Prochowska-Klisch, A. Podgórecka, J. Therm. Anal. 34 (1988) 203.
[4] J. Ghose, A. Kanungo, J. Therm. Anal. 20 (1981) 459.
[5] J. Mu, D.D. Perlmutter, Thermochim. Acta 56 (1982) 253.
[6] C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963, p. 494.
[7] D. Nikolova, M. Maneva, J. Therm. Anal. 44 (1995) 469.
[8] P. Bérnard, J.P. Auffrédic, D. Louër, Mater. Sci. Forum 79–82 (1991) 709 (EPDIC 1, Pt. 2).
[9] B.V. L'vov, A.V. Novichikhin, Spectrochim. Acta B 50 (12) (1995) 1427.
[10] J.G. Jackson, A.V. Novichikhin, R.W. Fonseca, J.A. Holcombe, Spectrochim. Acta B 50 (12) (1995) 1423.
[11] J.G. Jackson, R.W. Fonseca, J.A. Holcombe, Spectrochim. Acta B 50 (12) (1995) 1449.
[12] F.W. McLaffery, D.B. Stauffer, The Wiley/NBS Registry of Mass Spectral Data, vol. 1, Wiley, New York, 1998, p. 3.
[13] K.H. Stern, J. Phys. Chem. Ref. Data 1(3) (1972) 751.
[14] S. Murata, M. Sakiyama, S. Seki, Thermochim. Acta 88 (1985) 121.
[15] G.A. Semenov, E.N. Nikolaev, K.E. Frantseva, Application of Mass Spectrometry in Inorganic Chemistry, Khimiya, Leningrad, 1976 (in Russian).
[16] C. Duval, Anal. Chim. Acta 20 (1959) 264.