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THE THERMAL DEHYDRATION, DECOMPOSITION AND KINETICS OF $Mn(NO_3)_2 \cdot 6H_2O$ AND ITS DEUTERATED ANALOGUE

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The processes of thermal dehydration and decomposition of $Mn(NO_3)_2 \cdot .6H_2O$ and its deuterated analogue were studied by DTA, TG and DSC. Comparisons were made between the data obtained for the two compounds. The following phase transitions were observed: melting of the compound; dehydration to monohydrate; dehydration of the monohydrate, accompanied by its partial decomposition to MnO_2; and decomposition of the anhydrous nitrate to MnO_2.

The DSC data were used to determine the enthalpies of the phase transitions, and those corresponding to the partial dehydration were compared with the calculated ones. The formal kinetic parameters (E^* and A) for the three stages (without the melting stage) were calculated from the TG curves, and the corresponding kinetic equations are reported.

The pertinent literature contains data about the thermal decomposition of aqueous solutions of $Mn(NO_2)_2$. According to [1-3], for instance, the water is evaporated until the formation of a solution containing $Mn(NO_3)_2$ and H_2O in a mole ratio of 1:1, whereas [4, 5, 9, 10] give this mole ratio as 1:2. This is followed by decomposition of the nitrate to MnO_2, which according to [1, 2, 4, 9] takes place in one stage, whereas other authors have recorded intermediates: Mn(III) oxynitrate [5]: a mixture of MnO_2 and $Mn(NO_3)_2$ [3]: or unstable $Mn(OH)_2NO_3$, MnOOH and amorphous MnO_2 [10]. The thermal decomposition of $Mn(NO_3)_2 \cdot 6H_2O$ has been studied in [8], with the authors describing fusion of the salt, dehydration to $Mn(NO_3)_2 \cdot 1.7H_2O$ and decomposition to MnO_2.

All authors report MnO_2 as the end-product of the thermal decomposition, but according to [10] it contains impurities of Mn_2O_3.

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In [11] there are some thermodynamic computations, and the DTA curve data were used to determine the enthalpies of the phase transitions examined in [3].

Formal kinetic parameters relating to the thermal decomposition of aqueous solutions of $Mn(NO_3)_2$ have been calculated in [4, 6, 12, 13], the results presented in [12] being based on thermogravimetric data.

The objectives of the present study, based on the reference data, were as follows:

a. To study the non-isothermal dehydration and decomposition of ordinary and deuterated crystalline manganese(II) nitrate hexahydrate in an atmospheric medium, at two different rates of heating, and to compare the characters and the temperatures of the phase transitions for the two compounds.

b. In order to clarify the chemistry of the process, to isolate and identify intermediate samples taken at temperatures corresponding to important phase transitions.

c. To investigate the influence of the mass of the initial sample on the degree of decomposition of the nitrate to MnO_2.

d. By means of DSC to determine the enthalpies of the phase transitions, involving comparisons for the two compounds and with the calculated enthalpies.

e. To calculate the formal kinetic parameters for the individual stages of thermal dehydration and decomposition.

Experimental

The initial $Mn(NO_3)_2 \cdot 6H_2O$ was obtained by twofold recrystallization of $Mn(NO_3)_2 \cdot 6H_2O$ reagent of p.a. grade, while its deuterated analogue was obtained by severalfold recrystallization of lower hydrates from heavy water (99.9%). The latter were obtained upon vacuum treatment of the hexahydrate at 40-50°. The two compounds were kept under argon at 10° and were identified by quantitative analysis:

Mn – complexometrically [14], NO_3^- - spectrophotometrically on a Perkin-Elmer 323 instrument, and water - by Fisher's method [15].

Depending on the problems to be solved, a number of apparatuses were used in the thermal investigations: Linseis thermogravimetric balance and MOM - Budapest and Netzsch-429 derivatographs. The DTA and TG curves were taken with a MOM apparatus at heating rates of 2 deg/min and

5 deg/min, in open ceramic crucibles, from 20° and 250° with a sample weight of 300 mg. The influence of the mass of the initial sample on the amount of MnO_2 contained in one of the intermediate samples was investigated with the Linseis thermogravimetric balance, at sample weights of 10, 20, 30, 100 and 150 mg, while the influence of the shape of the crucible was investigated with the Netzsch-429 apparatus. The intermediate samples were isolated at 20°, 150°, 190° and 210°, at a heating rate of 2 deg/min, with an initial sample weight $m = 100$ mg; they correspond to inflexion points in the TG curves. They were identified by quantitative analysis for the contents of Mn^{2+} and Mn^{4+} [10], NO_3^- groups and water (by Fisher's method). The diffractogram of the oxide obtained as end-product was taken with a Philips apparatus with α-Cu irradiation.

The enthalpies of the phase transitions observed were determined with a Metler-3000 DSC apparatus at a heating rate of 5 deg/min, in perforated aluminium crucibles.

The formal kinetic parameters for the individual stages in the thermal decompositions of the investigated compounds were calculated on the basis of the data from the TG curves taken with the Linseis apparatus at a heating rate of 5 deg/min and an initial sample weight of 100 mg.

Experimental data and discussion

The DTA and TG curves for $Mn(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6D_2O$ are presented in Fig. 1. The temperatures of the phase transitions obtained from the DTA and TG curves and the changes in the sample weight are given in Table 1. The quantitative analysis data on the compositions of the intermediate samples taken at points *B* and *C* in Fig. 2 are listed in Table 2.

Figure 2 presents the TG curves of samples with an initial mass of 100 mg and a heating rate of 5 deg/min, while Fig. 3 shows the dependence between the amount of the initial sample and the percentage content of MnO_2 at point *C* (Fig. 2), obtained in the decomposition of the intermediate sample. The DSC data are collected in Table 3.

The thermoanalytical curves in Fig. 1 (*a* and *b*) show a small endoeffect at 32° for $Mn(NO_3)_2 \cdot 6H_2O$ and at 30° for $Mn(NO_3)_2 \cdot 6D_2O$, which corresponds to the melting points of the two compounds. Immediately after this, the TG curve shows a decrease in the mass of the sample, and DTA reveals a second endoeffect with maximum at 150° for the ordinary hydrate and at 145° for the deuterated one. The decrease in mass corresponding to this effect is Δ*m* =31.5% and 33.5%, respectively (Table 1), i.e. very close to the theoretical change in mass calculated for the transition

$$Mn(NO_3)_2 \cdot 6H_2O \rightarrow Mn(NO_3)_2 \cdot H_2O + 5H_2O \qquad (1)$$

or that of the deuterated analogue (Table 1). The course of the indicated dehydration process is confirmed by the quantitative analysis data on the composition of the intermediate sample isolated at 150° and Δ*m* =31.5% (Table 2 and Fig. 1, curve a, point B).

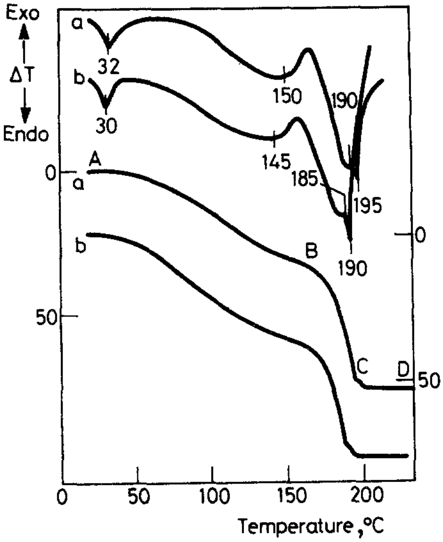

Fig. 1 DTA and TG curves of $Mn(NO_3)_2 \cdot 6H_2O$ (a) and $Mn(NO_3)_2 \cdot 6D_2O$ (b) at $V=2$ deg/min and $m=300$ mg

The end of the described process is the beginning of a new one manifested in the DTA curves (Fig. 1) with a large endoeffect and two maxima, at 190° and 195° for $Mn(NO_3)_2 \cdot 6H_2O$ and at 185° and 190° for $Mn(NO_3)_2 \cdot 6D_2O$. Its character shows that in this case there are two processes, this being in accord with the course of the TG curves, namely: a sharp change in their course at Δ*m* =67.1% for the ordinary hydrate and at Δ*m* =67.9% for the deuterated one (Table 1, point C). On comparison of these curves with the TG curves taken for samples with a mass of 100 mg (Fig. 2), we find the inflexion at a different Δ*m*, namely Δ*m* =62% for $Mn(NO_3)_2 \cdot 6H_2O$ and Δ*m* =62.5% for $Mn(NO_3)_2 \cdot 6D_2O$. This accounts for the existing interest in investigations of the influence of the initial samples mass on the composition of the intermediate sample corresponding to the inflexions in the TG curves (Fig. 2, point *C*).

Table 1 Data from the DTA and TG curves for $Mn(NO_3)_2\cdot 6H_2O$ and $Mn(NO_3)_2\cdot 6D_2O$ at V = 2 deg/min

Phase transition	Form	Δm_{theor}, %	Δm_{exp}, %	$T_{init.}$	$T_{fin.}$	$T_{max.}$
				°C (DTA)		
$Mn(NO_3)_2\cdot 6H_2O$ (sol.) → $Mn(NO_3)_2\cdot 6H_2O$ (liq.)	H	0.0	0.0	25	50	32
	D	0.0	0.0	25	45	30
$Mn(NO_3)_2\cdot 6H_2O$ (liq.) → $Mn(NO_3)_2\cdot H_2O + 5H_2O$	H	31.4	31.5	50	165	150
	D	33.5	33.5	45	150	145
$nMn(NO_3)_2\cdot H_2O$ → $(n\text{-}1)Mn(NO_3)_2 + MnO_2 + 2NO_2 + nH_2O$	H		67.1	165		190
	D		67.9	160		185
$(n\text{-}1)Mn(NO_3)_2$ → $(n\text{-}1)MnO_2 + 2(n\text{-}1)NO_2$	H	69.7	69.7		220	195
	D	70.9	71.0		215	190

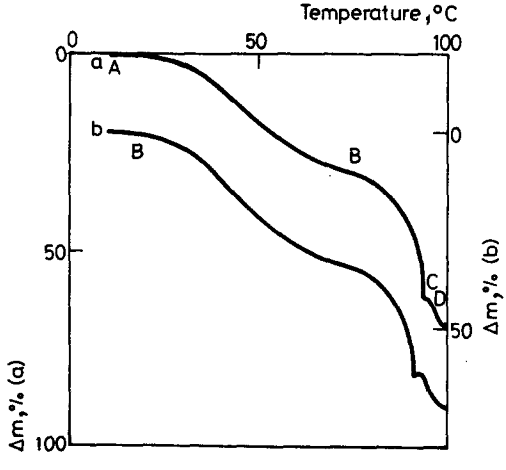

Fig. 2 TG curves of a - $Mn(NO_3)_2\cdot 6H_2O$ and b - $Mn(NO_3)_2\cdot 6D_2O$; m = 100 mg

To this end, TG curves were taken of samples with masses of 10, 20, 50, 100 and 150 mg, and Fig. 3 presents the dependence established. It shows that, with increase of the initial sample mass, the inflexion shifts towards

Table 2 Quantitative analysis data on the samples taken in the thermal dehydration and decomposition of $Mn(NO_3)_2 \cdot H_2O$ at $V = 2$ deg/min and an initial sample weight of 100 mg

No. of	Δm,	T,	Chemical composition				Molar ratio
sample	%	°C	Mn^{2+}	Mn^{4+}	NO_3^-	H_2O	$Mn^{2+}:Mn^{4+}:NO_3^-:H_2O$
1 (A)	0.0	20	19.1	0.0	43.2	37.6	1.0:0.0 : 2.0:6.0
2 (B)	31.5	150	27.9	0.0	63.0	9.1	1.0:0.0 : 2.0:1.0
3 (C)	61.9	190	12.1	38.2	27.4	0.0	1.0:3.2 : 2.0:0.0
4 (D)	69.7	210	0.0	63.2	0.0	0.0	0.0:1.0 : 0.0:0.0

larger values of Δm, the change being most essential in the interval 10-50 mg.

In order to explain the chemistry of the process in the examined stage, a sample was isolated at the point where the TG curve changes its course (Fig. 2, point *C*) at 190°, and it was identified quantitatively. The data obtained are presented in Table 2, point *C*. On the basis of these data, the following chemical behaviour of the process taking place in the interval *BC* of the TG curve is most probable (Fig. 2, curve *a*):

$$n\mathrm{Mn(NO_3)_2 \cdot H_2O} \rightarrow (n-1)\mathrm{Mn(NO_3)_2} + \mathrm{MnO_2} + 2\mathrm{NO_2} + n\mathrm{H_2O}$$

In fact, on the action of the water released in the dehydration of the monohydrate, the $Mn(NO_3)_2$ obtained partially decomposes to MnO_2, and consequently at point *C* in Fig. 2 two different solid phases exist: $Mn(NO_3)_2$ and MnO_2. The amount of MnO_2 obtained, i.e. Δm of the sample, differs

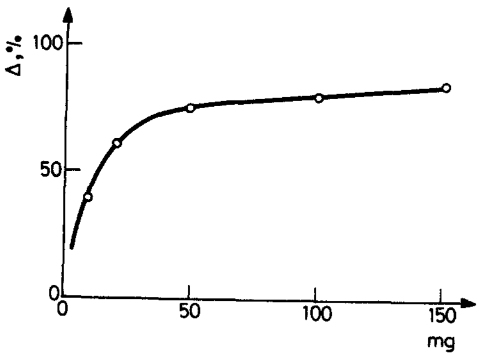

Fig. 3 Dependence between the degree of decomposition of the initial $Mn(NO_3)_2 \cdot 6H_2O$ and its mass

depending on the initial sample mass (Fig. 3). By relating the chemistry of the thermal decomposition of $Mn(NO_3)_2 \cdot H_2O$ to the established dependence for the influence of the initial sample mass (Fig. 3), we obtain confirmation of the assumption made in [3, 5] that water has a favourable effect on the process of decomposition of $Mn(NO_3)_2$. Increase of the initial sample mass (Fig. 3) is accompanied by an increase in the amount of $Mn(NO_3)_2$ decomposed on the action of water, i.e. the TG curves change their course at higher values of Δm. Such a change in the course of the curves is not observed with masses of 375-400 mg, and this can be explained by the greater amount of water released, which is sufficient for the complete decomposition of $Mn(NO_3)_2$ to MnO_2.

Confirmation of the role played by water may be the fact we have established that when small-diameter crucibles are used the decomposition of the nitrate takes place in one phase, even for samples with a mass considerably smaller than 375 mg. This may be explained by the conditions of the experiment, whereby there is a longer contact between the dehydration water released and the $Mn(NO_3)_2$.

A comparison of the DTA curves for the ordinary and deuterated samples shows that the endoeffects in the thermal decomposition of $Mn(NO_3)_2 \cdot 6H_2O$ are at temperatures 5-10 deg higher than the analogous temperatures for $Mn(NO_3)_2 \cdot 6D_2O$.

The DSC curves of both compounds show three endoeffects. If these are compared with the DTA data, they may be attributed to the following phase transitions: dehydration of the hexahydrate to $Mn(NO_3)_2 \cdot H_2O$; dehydration of $Mn(NO_3)_2 \cdot H_2O$ to $Mn(NO_3)_2$, accompanied by partial decomposition of the latter to MnO_2; and decomposition of the remaining $Mn(NO_3)_2$ to MnO_2. It is not possible to register the endoeffect of melting, since both compounds melt at temperatures below those at which the apparatus begins to record the thermal effects. The temperatures and the enthalpies of the phase transitions are presented in Table 3.

The enthalpy of decomposition $Mn(NO_3)_2 \cdot H_2O$ to MnO_2 (second and third endoeffects) is $\Delta H^0 = 163$ kJ/mol and is similar to the enthalpy for the same process calculated from the DTA curves: $\Delta H^0 = 170 \pm 14$ kJ/mol according to [11]. For the deuterated sample, the enthalpy corresponding to the second endoeffect ($\Delta H^0 = 102$ kJ/mol) is smaller than the one corresponding to $Mn(NO_3)_2 \cdot 6H_2O$ ($\Delta H^0 = 126$ kJ/mol). The difference arises from the fact that a larger amount of $Mn(NO_3)_2$ undergoes decomposition on the action of H_2O, as compared to the case involving D_2O, a fact confirmed by the TG curves (Figs 1 and 2) in which the section *CD* for $Mn(NO_3)_2 \cdot 6H_2O$ is larger than the corresponding one for $Mn(NO_3)_2 \cdot D_2O$.

Table 3 DSC data for $Mn(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6D_2O$, at a heating rate of 5 deg/min

Phase transition	H form, °C			ΔH^0	D form, °C			ΔH^0
	$T_{in.}$	$T_{ter.}$	T_{max}	kJ/mol	$T_{in.}$	$T_{ter.}$	T_{max}	kJ/mol
$Mn(NO_3)_2 \cdot 6H_2O$ (sol.) → $Mn(NO_3)_2 \cdot 6H_2O$ (liq.)	-	-	-	-	-	-	-	-
$Mn(NO_3)_2 \cdot 6H_2O$ (liq.) → $Mn(NO_3)_2 \cdot H_2O + 5H_2O$	40	165	112	169	40	160	102	181
$nMn(NO_3)_2 \cdot H_2O$ → $(n-1)Mn(NO_3)_2 + MnO_2 + nH_2O + 2NO_2$	165	195	192	126	160	198	182	102
$(n-1)Mn(NO_3)_2$ → $(n-1)MnO_2 + 2(n-1)NO_2$	195	215	204	37	188	215	204	55

In the course of our studies we also determined the enthalpy of dehydration of the hexahydrate to monohydrate, whose value for $Mn(NO_3)_2 \cdot 6H_2O$ is $\Delta H^0 = 169$ kJ/mol, while for the deuterated analogue it is $\Delta H^0 = 181$ kJ/mol. There are no analogous data in the pertinent literature connected with investigations of crystalline $Mn(NO_3)_2 \cdot 6H_2O$, while those we have obtained by means of DSC have been compared with those calculated after Hess for the dehydration process in the cases when the hydrate water released is in the liquid or the vapour state:

For $Mn(NO_3)_2 \cdot 6H_2O$ (after Eq. 1):

$$\Delta H^0_{\text{dehpr.}} = 294 \text{ kJ/mol (for } H_2O \text{ gas)}$$

$$\Delta H^0_{\text{dehpr.}} = 75 \text{ kJ/mol (for } H_2O \text{ liquid)}$$

For $Mn(NO_3)_2 \cdot 6D_2O$ (after Eq. 1):

$$\Delta H^0_{\text{dehpr.}} = 307 \text{ kJ/mol (for } D_2O \text{ gas)}$$

$$\Delta H^0_{\text{dehpr.}} = 80 \text{ kJ/mol (for } D_2O \text{ liquid)}$$

As compared to the data obtained experimentally, the computed data indicate that under the conditions of the experiment the hydrate water evolved is only partially in the gaseous state. The ratio of the values obtained for the enthalpies of the ordinary and deuterated hydrates is close to the computed one ($\frac{\Delta H^0_H}{\Delta H^0_D}$ varies from 0.93 to 0.95), which confirms the fact that dehydration to monohydrate takes place within the system.

The formal kinetic parameters for the thermal decomposition of the two compounds were also calculated on the basis of the TG curves (Fig. 2), by using the general differentiation method. These parameters were calculated separately for the three phases examined and are presented in Table 4.

Table 4 Kinetic parameters for the thermal dehydration and decomposition of $Mn(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6D_2O$

Stage	H form		D form	
	E^*, kJ/mol	A, s^{-1}	E^*, kJ/mol	A, s^{-1}
I	34	$6.1 \cdot 10^5$	39	$5.6 \cdot 10^6$
II	127	$2.2 \cdot 10^{13}$	120	$2.5 \cdot 10^{13}$
III	112	$1.3 \cdot 10$	104	$8.6 \cdot 10^{12}$

The stage of dehydration of the hexahydrate to monohydrate (stage I) for the *H* and *D* forms can be described by the kinetic equation

$$f(\alpha) = \alpha^{2/3}$$

i.e. the equation of the accelerating type exponential law.

For the second stage (II), corresponding to the first stage of decomposition of the nitrate-monohydrate, the kinetic equation of the following type was chosen as the most suitable one:

$$f(\alpha) = \alpha$$

The thermal dehydration of the two hexahydrates to monohydrate can be described by the kinetic equation

$$f(\alpha) = (1-\alpha)^{1/2}$$

This equation is of the accelerating type exponential law.

For the first stage of decomposition of the nitrate, the authors of [6, 13] offer the equation of Avrami-Erofeev and accordingly compute $E^* = 90$ kJ/mol and $E^* = 120$ kJ/mol. The latter is very close to our computed value of $E^* = 127$ kJ/mol.

For the second stage of thermal decomposition (stage III), both in [6] and under the conditions of our experiment, the most suitable kinetic equation selected is the one based on the geometric model of a contracting surface.

The authors in [6] point out that, on elevation of the concentration of water vapour, the activation energy can be reduced form $E^* = 122\text{-}139$ kJ/mol to $E = 76\text{-}83$ kJ/mol. This is in full correlation with the value we have obtained: $E^* = 112$ kJ/mol.

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Zusammenfassung – Mittels DTA, TG und DSC wurde der Verlauf der thermischen Dehydratation und Zersetzung von deuteriertem und undeuteriertem $Mn(NO_3)_2 \cdot 6H_2O$ untersucht und die erhaltenen Ergebnisse beider Verbindungen miteinander verglichen. Folgende Phasenumwandlungen konnten beobachtet werden: Schmelzen der Verbindung; Dehydratation bis zum Monohydrat; Dehydratation des Monohydrates unter teilweiser Zersetzung zu MnO_2; Zersetzung von wasserfreiem Nitrat zu MnO_2.

DSC-Daten wurden zur Bestimmung der Enthalpien für die Phasenumwandlungen benutzt, die so ermittelten Ergebnisse für die partielle Dehydratation wurden mit den berechneten verglichen. Anhand der TG-Kurven wurden die formellen kinetischen Parameter (E^* und A) der drei Schritte (ohne Schmelzvorgang) berechnet und die entsprechenden kinetischen Gleichungen beschrieben.