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THERMAL ANALYSIS OF MANGANESE(II) COMPLEXES WITH *L*-PROLINE AND *L*-HYDROXYPROLINE

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Abstract

The thermal decomposition reactions of manganese(II) complexes with *L*-proline and 4-hydroxy-*L*-proline were studied. The Mn(II) proline complex loses the water molecule at 40–95°C and then, heated above 250°C it decomposes in several steps to manganese oxide. The most appropriate kinetic equations for dehydration process are the geometrical R2 or R3 ones. They give a value of activation energy, E of about 95 kJ mol^{-1}. The Mn(II) hydroxyproline complex loses the water molecules in two stages (70–110 and 110–230°C) and next it decomposes to manganese oxide in several steps. The R3 or D3 (three-dimensional diffusion) models are the most appropriate for the first stage of dehydration (E is about 155 kJ mol^{-1}). The second step of dehydration is limited by D3 mechanism (E=52 kJ mol^{-1}).

Keywords: amino acids, dehydration, manganese(II) complexes, kinetics in solid state, TG

Introduction

There are considerable discussions in the literature concerning the validity of the kinetic data obtained by non-isothermal experiments. It is difficult to interpret the kinetic parameters, such as activation energy and pre-exponential factor, for the reaction in solid state. Very often the kinetic calculation do not permit to indicate only one kinetic model, but it is possible to choose two or three most probable models among all mentioned in literature. The non-isothermal TG methods have also an advantage: one TG curve is equivalent to a larger number of isothermal mass loss curves.

The present paper is a part of our research concerning the complexes of manganese(II) with amino acids. The purpose of this work was to study the thermal decomposition of the manganese(II) complexes with *L*-proline and 4-hydroxy-*L*-proline and to compare the way of dehydration and decomposition with the crystal structure of compounds.

Experimental

The preparation and the way of the crystal structure investigation of examined complexes have been described before [1, 2]. The thermal decomposition of the compounds was in-

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vestigated by means of several techniques. The simultaneous TG-DTG-DTA curves were recorded in static air atmosphere using a Q 1500D derivatograph (sample mass=50, 100 mg, β=2.5, 5, 10 K min^{-1}). In order to achieve a better separation of particular stages of decomposition a high resolution TG technique was used. TG and DTG curves were recorded in static air and in flowing nitrogen (v=4–6 dm^3 h^{-1}, sample mass=7–20 mg) using a Hi-Res-TA apparatus (TA Instruments). The simultaneous TA-infrared system was used to determine the gaseous products of thermal decomposition. A Netzsch TG 209 apparatus connected with a Bruker FTIR spectrophotometer were used (sample mass=14 mg, β=20 K min^{-1}, flowing argon atmosphere).

Results and discussion

The manganese(II) complex with *L*-proline with the formula $[MnCl_2(C_5H_9NO_2)]{\cdot}H_2O$ crystallises in the orthorhombic space group $P2_12_12_1$. The manganese ions are connected in the polymeric chain by two chloride bridges and by one bridge formed by carboxylate groups. The water molecule participates in three hydrogen bonds: as a proton donor to a chlorine atom and to an oxygen atom from a carboxylate group and as a proton acceptor from a proline NH_2 group. The bonds with the chlorine or oxygen atoms are very weak and the third mentioned bond is moderately strong [1]. The proline complex is stable up to 40°C and heated loses the water molecule. The anhydrous salt is stable up to 250°C and then it decomposes in several steps forming Mn_3O_4 in air or MnO in inert atmosphere (Table 1). The analysis of the gaseous products of thermal decomposition confirms that the dehydration is the first stage of the reaction. Above 250°C one can detect the carbon dioxide and water molecules in IR spectra. The ammonia is evolved at higher temperature than it is observed in the case of the thermal decomposition of pure *L*-proline. The presence of manganese ions probably causes the coordination of a nitrogen atom and the formation of an intermediate solid product containing nitrogen.

The activation energy, E and pre-exponential factor, A of the dehydration process were calculated by means of differential equations (Table 2) [3]. The equation $\ln(d\alpha/dT)-\ln(f(\alpha))=\ln(A/\beta)-E/RT$ (where α is the fraction reacted, T – temperature in K, β – the rate of heating, R – the molar gas constant, $f(\alpha)$ is a mathematical expression in α due to the mechanism of reaction) was availed for β=5 K min^{-1}. The plot of the left side of equation *vs*. $1/T$ was drawn and in the case of linear plot the activation energy was obtained from the slope, and A from the intercept. Very good linearity was obtained for diffusion equations (Dn) as well as for geometric ones (Rn) (Table 2). However, the E values calculated for Dn models are almost twice as large as the geometrical model values. The hydration water molecule in the complex is in the outer co-ordination sphere and it is lost just above 40°C. This fact suggests the choice of smaller E values and R2 or R3 mechanism of dehydration. The E values calculated by means of these models are in good agreement with the literature data of activation energy values for the loss of outer sphere water molecules [4, 5].

Table 1 Thermal decomposition data of the manganese(II) complexes with proline and hydroxyproline in air and nitrogen atmosphere obtained by high resolution technique (*L* – proline, *L’* – hydroxyproline)

Air					Nitrogen				
Compound	Range of decomp./°C	Mass loss/%		Product	Compound	Range of decomp./°C	Mass loss/%		Product
		found	calc.				found	calc.	
$[MnLCl_2]\cdot H_2O$	40–95	6.85	6.95	$[MnLCl_2]$	$[MnLCl_2]\cdot H_2O$	40–95	6.95	6.95	$[MnLCl_2]$
$[MnLCl_2]$	250–400	37.00			$[MnLCl_2]$	240–400	48.20		
	410–510	70.50	70.50	Mn_3O_4		450–620	67.00		
						640–850	73.00	72.59	MnO
$[MnL'(H_2O)_4]SO_4$	70–110	12.30	12.71	$[MnL'(H_2O)_{1.5}]SO_4$	$[MnL'(H_2O)_4]SO_4$	70–110	12.30	12.71	$[MnL'(H_2O)_{1.5}]SO_4$
$[MnL'(H_2O)_{1.5}]SO_4$	110–230	20.60	20.34	$MnL'SO_4$	$[MnL'(H_2O)_{1.5}]SO_4$	110–230	20.60	20.34	$MnL'SO_4$
$MnL'SO_4$	240–440	48.50			$MnL'SO_4$	240–340	36.00		
	440–500	59.50	57.30	$MnSO_4$		340–360	40.00		
$MnSO_4$	670–780	76.80	77.68	Mn_2O_3		360–480	52.50		
Mn_2O_3	900–920	77.80	78.44	Mn_3O_4		500–600	78.00	79.94	MnO

The complex of manganese(II) with *trans*-4-hydroxy-*L*-proline of the formula $[Mn(C_5H_8NO_3)(H_2O)_4]SO_4$ was obtained. The compound crystallises in the triclinic system (space group P1). The Mn(II) ions are six-fold co-ordinated being surrounded by two carboxyl oxygen atoms and four water molecules. The sulphate anion is in outer co-ordination sphere, anchored exclusively via hydrogen bonds with water molecules. The carboxylate group bridges two adjacent Mn(II) ions and links to a polymeric chain [2]. All water molecules are located in inner sphere of complex, nevertheless the dehydration process is two-stage. The first stage begins above 70°C and the mass loss corresponds to the loss of 2.5 water molecules (Table 1). In the second stage (110–230°C) the remaining water molecules are lost. The anhydrous compound is stable in a very narrow temperature range. Heated above 240°C it decomposes in several steps and Mn_3O_4 in air or MnO in nitrogen or argon atmosphere are obtained. The analysis of gaseous product confirms that only water molecules are lost below 240°C. Above 260°C the IR bands of CO_2 and NH_3 appear. The thermal decomposition of the manganese complex was compared with the decomposition of the pure hydroxyproline. When the hydroxyproline decomposes the ammonia is detected in degradation products just above 270°C, and when the manganese complex is heated the NH_3 molecules are recorded above 310°C. One can again draw a conclusion that the nitrogen atom is co-ordinated by manganese ion in a solid intermediate product.

The activation energy of two stages of dehydration reaction was calculated. In the case of the first stage the D3 and R3 models fit the experimental results best. The results obtained by use of the both models are equal. It is probable that the rate of the process is limited by chemical reaction as well as by diffusion. Three-dimensional diffusion also determines the rate of the second step of dehydration (Table 2). Figure 1 presents the curves of the complementary extent of dehydration $(1-\alpha)$ of Mn(II) hydroxyproline complex as a function of temperature at $\beta=5$ K min^{-1}. The b and d lines present the real curves obtained by TG analysis for the first and second step of dehydration, respectively. The a, c and e lines are the hypothetical curves calculated for the kinetic models fitting the real curves best. The values of curve a are calculated for R3 model (E=154.6 kJ mol^{-1}; A=1.15·10^{19} min^{-1}). The values of curve a are calculated for R3 model (E=154.6 kJ mol^{-1}; A=1.15·10^{19} min^{-1}), curve c – for D3 model (E=158.6 kJ mol^{-1}; A=1.23·10^{19} min^{-1}) and the curve e is obtained for second step of dehydration for D3 model (E=52.1 kJ mol^{-1}; A=4.12·10^{5} min^{-1}).

The activation energy of the first stage of dehydration is large (above 150 kJ mol^{-1}). This fact has its confirmation in the structure of the compound, because the water molecules are in the inner sphere of the complex. The E value of the second stage is significantly lower (about 50 kJ mol^{-1}). It is possible that the first stage of dehydration causes such a change in the compound structure that the remaining water molecules are weakly linked. The diffusion mechanism of the second step of dehydration was expected. The reaction occurs above 110°C. At such temperature the process of the loss of water is quick and usually the diffusion of the liberated water molecules by reactant layers determines the rate of dehydration.

It was mentioned above that all water molecules in hydroxyproline complex of manganese were connected directly with manganese ions. The Mn–O distances are

Table 2 Activation energy, *E* and pre-exponential factor, *A* values of dehydration reaction of manganese(II) complexes with proline and hydroxyproline (α – fraction decomposed, *r* – correlation coefficient)

Kinetic model	$[Mn(pro)Cl_2]{\cdot}H_2O$			$[Mn(hpro)(H_2O)_4]SO_4$					
	$\alpha\in(0.06; 0.83)$			$-2.5H_2O$ $\alpha\in(0.07; 0.90)$			$-1.5H_2O$ $\alpha\in(0.06; 0.90)$		
	E/kJ mol^{-1}	A/min^{-1}	r	E/kJ mol^{-1}	A/min^{-1}	r	E/kJ mol^{-1}	A/min^{-1}	r
F1	110.5	$1.60{\cdot}10^{17}$	0.98926						
F2	176.7	$1.82{\cdot}10^{28}$	0.97972	172.8	$1.58{\cdot}10^{21}$	0.95554	62.3	$2.17{\cdot}10^{7}$	0.96854
F3	259.5	$2.21{\cdot}10^{42}$	0.95869	184.6	$9.76{\cdot}10^{22}$	0.96938	103.2	$1.54{\cdot}10^{13}$	0.96120
R2	92.5	$7.53{\cdot}10^{13}$	0.99396	155.7	$4.52{\cdot}10^{18}$	0.96301			
R3	97.9	$4.12{\cdot}10^{14}$	0.99216	154.6	$1.15{\cdot}10^{19}$	0.97895			
D1	156.4	$1.47{\cdot}10^{24}$	0.99860	180.7	$1.89{\cdot}10^{22}$	0.91216			
D2	168.5	$8.41{\cdot}10^{25}$	0.99706	188.3	$2.34{\cdot}10^{23}$	0.93343	51.3	$2.71{\cdot}10^{5}$	0.89302
D3	186.1	$1.69{\cdot}10^{28}$	0.99566	158.6	$1.23{\cdot}10^{19}$	0.97884	52.1	$4.12{\cdot}10^{5}$	0.97324
D4	174.5	$1.90{\cdot}10^{26}$	0.99680	191.3	$5.50{\cdot}10^{23}$	0.94043	38.5	$5.81{\cdot}10^{4}$	0.93673
A2	64.6	$4.92{\cdot}10^{9}$	0.98636						
A3	48.4	$9.44{\cdot}10^{6}$	0.97997						

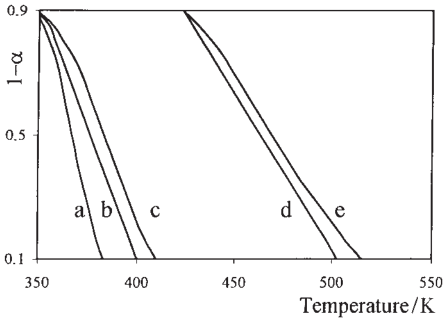

Fig. 1 Complementary extent of dehydration (1–α) of Mn(II) hydroxyproline complex as a function of temperature at β=5 K min^{-1} for the first stage (curve b) and second stage (curve d) and calculated for models R3 (curve a) and D3 (curve c) for the first stage and for model D3 (curve e) for the second stage of dehydration

within the range of 2.141(3)–2.255(2) Å. Additionally, any water molecule forms two O–H···O hydrogen bonds. The O···O distances range from 2.629(5) to 2.856(4) Å, and the O–H–O angles – from 146 to 180°. Examining the crystal structure of the complex one can suggest that in the first stage of dehydration the water molecules connected with manganese ions by longer bonds are lost (there are 5 such water molecules in one dimeric molecule of complex). It is also noticeable that the mentioned water molecules participate in weaker hydrogen bonds (longer O···O distances and smaller O–H–O angles) than the other.

Conclusions

1. The thermal decomposition of the manganese(II) complexes with *L*-proline and 4-hydroxy-*L*-proline begins by a dehydration process. The anhydrous compounds decompose above 250°C forming Mn_3O_4 in air and MnO in nitrogen. Probably, a solid intermediate product containing the nitrogen atom co-ordinated by manganese ion is formed.
2. The rate of dehydration process of manganese(II) complex with *L*-proline is probably limited by phase boundary reaction (R2 or R3 kinetic model).
3. The rate of the first dehydration step of manganese(II) complex with hydroxyproline is limited by phase boundary reaction (R3 kinetic model or by three-dimensional diffusion (D3). The second step of dehydration is limited by D3 mechanism.

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