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THERMAL DECOMPOSITION OF Mn(II) COMPLEX OF NICOTINAMIDE

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Abstract

The complex $Mn(Nica)_2Cl_2$ (Nica = nicotinamide) was prepared, and its decomposition was studied by means of TG and DSC. The IR spectra of the products of thermal decomposition were examined at every stage. Kinetic analysis of the first stage of thermal decomposition was performed via the TG-DTG curves, and the kinetic parameters were obtained from analysis of the TG-DTG curves with integral and differential methods. The most probable kinetic function was suggested from a comparison of the kinetic parameters. Mathematical expressions were derived for the kinetic compensation effect.

Keywords: Mn(II) complex, nicotinamide, non-isothermal kinetics

Introduction

Nicotinamide is a vitamin. It is an integral part of three different coenzymes, which act as prosthetic groups for a variety of metabolic enzymes. The main function of these enzymes lies in the area of biological oxidation-reduction. For a better understanding of the interactions of metal ions with nicotinamide in its biological environment, many stable complexes of metal salts with nicotinamide have been studied previously [1–4]. In the present paper, preparation of the Mn(II) complex of nicotinamide $Mn(Nica)_2Cl_2$ and the mechanism of thermal decomposition of $Mn(Nica)_2Cl_2$ were studied. The products of thermal decomposition of this complex were examined by means of their IR spectra at every stage. For the TG-DTG curve, the differential equation of Achar *et al.* [5] and the Coats-Redfern integral equation [6] were used to analyse the non-isothermal decomposition process. The integral and differential equations are as follows:

$$\ln \frac{g(a)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \tag{1}$$

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$$\ln\left(\frac{da/dt}{f(a)}\right) = \ln A - \frac{E}{RT} \quad (2)$$

where a is the fractional decomposition, T is the absolute temperature (K), da/dt is the reaction rate, A is the preexponential Arrhenius factor, β is the heating rate in deg·min^{-1}, E is the apparent activation energy (kJ·mol^{-1}), R is the gas constant in kJ·mol^{-1}·deg^{-1}, $f(a)$ and $g(a)$ are the differential and integral functions, respectively.

Experimental

Preparation of complex

A solution of nicotinamide (0.015 mol) in ethanol (40 ml) was refluxed with a solution of $MnCl_2 \cdot 4H_2O$ (0.03 mol) in ethanol (40 ml) for 3 h in N_2. The precipitated complex was in turn washed with ethanol and ether, and then dried in a vacuum desiccator. Found for $Mn(Nica)_2Cl_2$, ($Mn(C_6H_6N_2O)_2Cl_2$): C: 38.54(38.91), H: 3.22(3.24), N: 14.51(15.13), Cl: 18.64(19.16), Mn: 14.76(14.80). The IR spectrum of the complex $Mn(Nica)_2Cl_2$ suggests that it has an octahedral framework through polymerization involving metal-chloride bridging [7].

Experimental equipment and conditions

TG analysis of $Mn(Nica)_2Cl_2$ was carried out by using a Perkin-Elmer TGA-7 thermogravimetric analyser under a nitrogen atmosphere, at a flow rate of 40 ml·min^{-1} and a heating rate of 10.00 deg·min^{-1}. The amount of sample used was 2.168 mg, and the temperature range was 40–600°C.

IR spectra

The IR spectra of the products of thermal decomposition were examined on a Perkin-Elmer 983 infrared spectrophotometer (KBr plates, 4000–400 cm^{-1}) at every stage.

Results and discussion

Thermal decomposition process

The TG-DTG curves and DSC curves of $Mn(Nica)_2Cl_2$ are shown in Fig. 1. The TG-DTG curves indicate that the complex undergoes a three-stage decom-

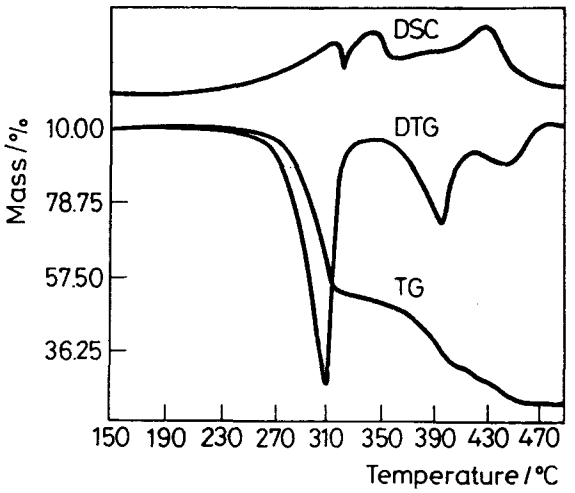

Fig. 1 TG-DTG curves and DSC curve of the process of thermal decomposition of $Mn(Nica)_2Cl_2$

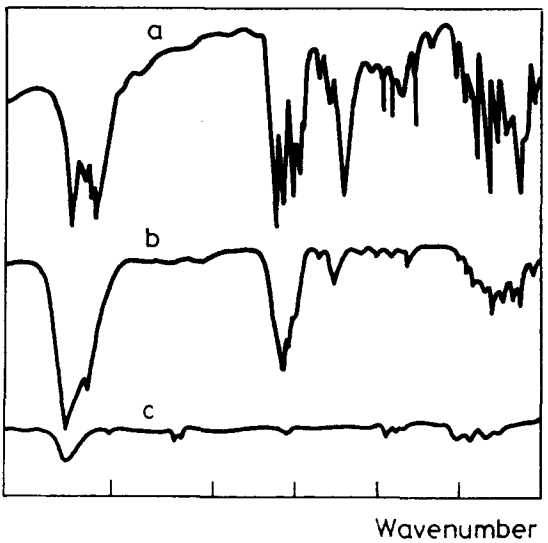

Fig. 2 IR spectra of (a) $Mn(Nica)_2Cl_2$, (b) the product of decomposition up to 330°C, and (c) the product of decomposition up to 411°C

position process. The DSC curves led to the same conclusion (there are three endothermic peaks in the DSC curve).

The IR spectra of the products of thermal decomposition at various stages were examined (Fig. 2). The IR spectrum of the residue after decomposition up to 330°C is similar to that of $Mn(Nica)_2Cl_2$ in the region 4000–400 cm^{-1}. The IR bands of nicotinamide are observed in the region 3200–3400 cm^{-1} for the

γ_{N-H} bands, at 1675 cm^{-1} for the $\gamma_{C=O}$ band and in the region 1577–1601 cm^{-1} for the C=C and C=N bands of the pyridine moiety. This shows that the nicotinamide molecule is still present in the tested substance. TG studies at this stage showed a mass loss corresponding to 4/3 molecules of nicotinamide. Thus, the probable product of decomposition at this stage is $Mn(Nica)_{2/3}ClOH$ (mass loss (%): calc.: 48.97, found: 48.80).

The IR spectrum of the product of decomposition up to 411°C is different from that of the complex $Mn(Nica)_2Cl_2$. The IR bands of nicotinamide are almost all lost. However, a band of γ_{O-H} is observed in the region 3300–3600 cm^{-1}. When this product was dissolved in dilute HNO_3 and a solution of $AgNO_3$ was added, a white precipitate of AgCl was formed, indicating that chloride ion is present in the substance. The substance is therefore considered to be MnOHCl (mass loss (%): calc.: 70.96, found: 70.95). However, chloride ion was not present in the final product of decomposition up to 481°C. The final substance is considered to be MnO (mass loss (%): calc: 80.81, found: 80.71). Thus, the thermal decomposition process of $Mn(Nica)_2Cl_2$ may be expressed by the following scheme:

$$Mn(Nica)_2Cl_2 \xrightarrow{230-330^\circ C} Mn(Nica)_{2/3}ClOH \xrightarrow{330-411^\circ C} MnOHCl \xrightarrow{411-481^\circ C} MnO$$

Nonisothermal kinetic study of the first decomposition process

The possible forms of $g(a)$ and $f(a)$ are listed in Table 1. The original TG-DTG data on the first stage of decomposition of $Mn(Nica)_2Cl_2$ are listed in Table 2.

With use of the possible forms of $g(a)$ and $f(a)$ in Table 1, the data in Table 2 were analysed by means of Eqs (1) and (2). The kinetic analyses were completed with the linear least squares method on an IBM computer. The results are shown in Table 3.

The results in Table 3 clearly show that the values of E and A obtained with the two methods are approximately the same. The linear correlation coefficient is better when the function is function No. 5 in Table 1. It can be concluded that the function of the probable mechanism of the first stage of decomposition of the complex $Mn(Nica)_2Cl_2$ is function No. 5 in Table 1. The kinetic equation of this process is

$$\frac{da}{dt} = A\exp\left(-\frac{E}{RT}\right) 3/2(1+a)^{2/3}\left[(1+a)^{1/3} - 1\right]^{-1}$$

Via the mathematical expression for the kinetic compensation effect $\ln A = a E + b$, the kinetic parameters (E and $\ln A$) are obtained with the inte-

gral and differential methods (for TG-DTG). Computation with the linear least squares method on a computer yields the kinetic compensation parameters a and b. The mathematical expression for the kinetic compensation effect is

$$\ln A = 0.2120\,E - 4.395 \quad r = 0.9973$$

Table 1 Kinetic functions used in the present analysis

Function	Function form	
No.	$g(a)$	$f(a)$
1	a^2	$1 / (2a)$
2	$a + (1 - a)\ln(1 - a)$	$-[\ln(1 - a)]^{-1}$
3	$(1 - 2a / 3) - (1 - a)^{2/3}$	$3[(1 - a)^{-1/3} - 1]^{-1} / 2$
4	$[1 - (1 - a)^{1/3}]^2$	$3(1 - a)^{2/3}[1 - (1 - a)^{1/3} - 1]^{-1} / 2$
5	$[(1 + a)^{1/3} - 1]^2$	$3(1 + a)^{2/3}[(1 + a)^{1/3} - 1]^{-1} / 2$
6	$[1 / (1 - a)^{1/3} - 1]^2$	$3(1 - a)^{4/3}[(1 / (1 - a)^{1/3} - 1)]^{-1} / 2$
7	$-\ln(1 - a)$	$(1 - a)$
8-11	$[-\ln(1 - a)]^n$ $(n = 2/3, 1/2, 1/3, 1/4)$	$(1 - a)[-\ln(1 - a)]^{-(n-1)} / n$
12-13	$1 - (1 - a)^n$ $(n = 1/2, 1/3)$	$(1 - a)^{-(n-1)} / n$
14-17	a^n $(n = 1, 1/2, 1/3, 1/4)$	$(1 - a)]^{-(n-1)} / n$
18	$(1 - a)^{-1} - 1$	$(1 - a)^2$
19	$(1 - a)^{-1/2}$	$2(1 - a)^{3/2}$

Table 2 TG-DTG data on the thermal decomposition of $Mn(Nica)_2Cl_2$

No.	T/K	a	da/dt
1	545.85	0.0917	0.1594
2	549.70	0.1123	0.2308
3	553.56	0.1420	0.3119
4	557.89	0.1828	0.4056
5	561.74	0.2317	0.5455
6	565.59	0.2961	0.6853
7	569.44	0.3765	0.8951
8	573.77	0.4970	1.1678
9	577.63	0.6268	1.4755
10	581.48	0.7711	1.6783
11	585.81	0.9195	1.4405

Table 3 Results of kinetic analysis of $Mn(Nica)_2Cl_2$

Function No.	Integral method			Differential method		
	E / kJ·mol^{-1}	ln A / s^{-1}	r	E / kJ·mol^{-1}	ln A / s^{-1}	r
1	307.83	59.10	0.9994	317.83	64.84	0.9951
2	337.05	64.85	0.9989	370.98	75.75	0.9994
3	349.21	66.07	0.9982	393.46	79.14	0.9989
4	374.08	71.57	0.9959	435.97	88.41	0.9954
5	280.44	50.77	0.9992	278.67	54.00	0.9907
6	459.10	90.31	0.9833	563.50	116.20	0.9779
7	202.37	37.76	0.9904	286.74	59.42	0.9840
8	131.78	22.62	0.9899	216.15	44.30	0.9810
9	96.49	14.96	0.9895	180.86	36.66	0.9784
10	61.19	7.15	0.9885	145.56	28.90	0.9742
11	43.54	3.13	0.9873	127.91	24.93	0.9710
12	173.22	30.55	0.9975	222.98	44.82	0.9981
13	182.34	32.19	0.9958	244.23	49.05	0.9944
14	149.22	25.85	0.9993	159.21	31.62	0.9836
15	69.91	8.83	0.9992	79.90	14.66	0.9427
16	43.47	2.94	0.9991	53.47	8.81	0.8858
17	30.25	-0.14	0.9990	40.25	5.84	0.8219
18	276.75	54.27	0.9625	414.28	87.21	0.9534
19	54.37	6.22	0.8077	350.51	72.62	0.9678

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Zusammenfassung — Der Komplex $Mn(Nica)_2Cl_2$ (Nica steht für Nikotinamid) wurde hergestellt und seine Zersetzung mittels TG und DSC untersucht. Die thermisch zersetzten Substanzen jedes Schrittes wurden mittels IR-Spektren untersucht. Anhand der TG-DTG-Kurven erstellte man eine kinetische Analyse des ersten Schrittes der thermischen Zersetzung, die kinetischen Parameter wurden aus den TG-DTG-Kurven unter Einsatz von Integrations- und Differentialmethoden ermittelt. Durch Vergleich der kinetischen Parameter wurde die wahrscheinlichste kinetische Funktion vorgeschlagen. Mathematische Ausdrücke für den kinetischen Kompensationseffekt wurden erhalten.