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STUDIES ON THE THERMAL DECOMPOSITION OF N,N'-ETHYLENEBIS(SALICYLIDENEIMINATO) DIAQUOCHROMIUM(III) NITRATE

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Abstract

A complex of N,N'-ethylenebis(salicylideneiminato)diaquochromium(III) nitrate, $[Cr(salen)(H_2O)_2]NO_3$ was characterized and its decomposition mechanism was studied by TG. The IR spectrum and X-ray analysis were examined for the complex. The non-isothermal kinetic data were analyzed by means of the Achar method and the Coats–Redfern method. The most probable kinetic model function was suggested by comparison of the kinetic parameters.

Keywords: Cr(III) complex, IR spectrum, non-isothermal kinetic, thermal decomposition, X-ray analysis

Introduction

It is known that chromium(III) is an essential nutrient that has been implicated as glucose tolerance factor (GTF) in the maintenance of normal carbohydrate and lipid metabolism [1–5]. Insufficient dietary intake of Cr is linked to increased risk factors associated with Type II diabetes and cardiovascular diseases. Several GTF model complexes have much higher biological activity. Schiff-base complexes of chromium(III) such as N,N'-ethylenebis(salicylideneiminato)diaquochromium(III) nitrate, $[Cr(salen)(H_2O)_2]NO_3$ was also a new kind of GTF model which has shown higher biological activity. Furthermore, Schiff-base complexes of chromium(III) have been employed to design and synthesize polynuclear complexes. So, they have played an important role in molecular magnetism [6]. Although the structure, the substitution reaction kinetics and some reactions of $[Cr(salen)(H_2O)_2]^+$ were studied previously [7–9], no thermal decomposition data have been reported in literatures for this complex. In this paper, we report a study of thermal decomposition and characterization of $[Cr(salen)(H_2O)_2]NO_3$ complex.

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Experimental

Preparation of complex

$[Cr(salen)(H_2O)_2]NO_3$ was prepared by standard method [6, 7], Salicylaldehyde (0.2 mol) and ethylenediamine (0.1 mol) were added to a solution of $Cr(NO_3)\cdot 9H_2O$ (0.16 mol) in ethylene glycol water-methanol (1:1:3.300 mL). After the mixture had been refluxed for 30 min, sodium carbonate (0.06 mol) was gradually added to the solution, followed by reflux of the solution for about 3~4 h. Concentrating the solution yielded a brown precipitate, which was recrystallized from 80% methanol to give brown crystals. Analysis for $[Cr(salen)(H_2O)_2]NO_3$ C: 49.20 (49.13); H: 4.41 (4.36); N:10.13 (10.09); Cr: 12.71 (12.49).

Thermal analysis

TG was carried out on a TGDTA92 multi-analyzer (Setaram Corp.). TG runs were carried out at a heating rate of 7.5°C min^{-1} under a dynamic nitrogen atmosphere using a flow rate of 40 mL min^{-1}, and the temperature range was 20–1000°C. The reference was α-Al_2O_3. Alumina crucibles were used to hold 8–10 mg samples for analyses.

IR analysis

The IR spectrum of the complex $[Cr(salen)(H_2O)_2]NO_3$ was examined on a Nicolet FT-IR spectrometer (using KBr pellets).

X-ray analysis

The X-ray analysis was carried out by means of a Siemens D/Max III B powder diffractometer, using CuK_α radiation. The sinters formed as a result of thermal decomposition. Figure 1 presents powder diffraction of the sinters.

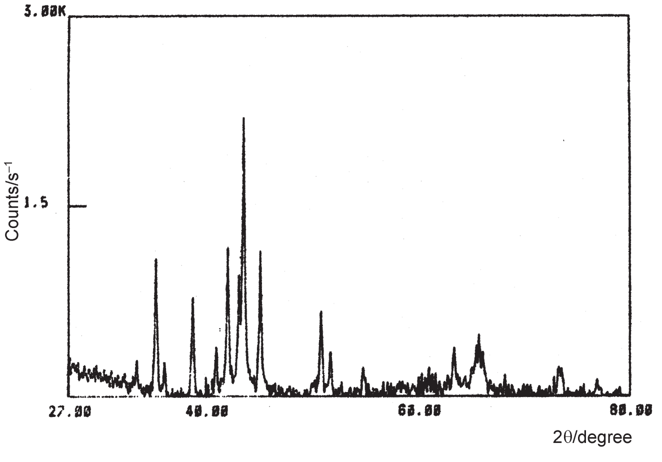

Fig. 1 X-ray of the decomposition product of the $[Cr(salen)(H_2O)_2]NO_3$

Molar conductance

The molar conductance was obtained with a DDS-11A conductivity detector. The complex is soluble in common solvents, such as water, methanol, alcohol, DMF, acetone, etc. The molar conductance in DMF solution is 100.0 S cm^2 mol^{-1} (298.15 K, $1.0\cdot10^{-3}$ mol^{-1}).

Element analysis

C, H and N contents were determined using a Perkin Elmer 240 elemental analyzer. The Cr content of the complex was determined according to the reported general procedure [10].

Results and discussions

IR spectrum

IR spectrum shows the absorption at 1630, 1598, 1577 and 1531 cm^{-1} attributable to C=N, C=C stretching frequencies of salen ligand and the absorption at 2600~3300 cm^{-1} attributable to coordination water molecules and $\gamma_{C\text{–}H}$ stretching frequencies. The absorption at 1380 cm^{-1} indicates that NO_3^- is not concerned with coordination. The IR bands around 387 and 376 cm^{-1} are assigned to $\gamma_{Cr\text{-}N}$, and the band at 514 cm^{-1} to $\gamma_{Cr\text{–}O}$ (phenolic), and the bands at 898, 542 and 499 cm^{-1} to ρ_r, ρ_w and $\gamma_{Cr\text{–}O}$ stretching frequencies of coordination water molecules [11]. These studies, as well as the molar conductance, infer that an octahedral structure of complex of chromium(III) is formed by the salen tetradentate Schiff base and two water ligands.

Thermal decomposition process

TG and DTG curves are shown in Fig. 2. These curves indicate that the compound $[Cr(salen)(H_2O)_2]NO_3$ undergoes a five-stage decomposition. The decomposition starts from 25 and ends at 160°C, the mass loss observed is 11.30 against the calculated 11.05%, corresponding to the release of one mole of NO_2. The second stage is in continuation with the first stage from 160 to 207°C. The mass loss observed is 3.96 against the calculated 4.33%, showing that one mole of water was expelled. The third stage is from 207 to 297°C. The mass loss observed is 8.80 against calculated loss of 8.65 %, corresponding to the release of two mole of water. The fourth stage is from 297 to 602°C. The mass loss observed is 25.98 against the calculated loss of 25.25%, due to the release of C_7H_5O. The last stage is from 602 to 977°C. The mass loss observed is 14.46 against the calculated loss of 14.67%, corresponding to the dissociation of C_2H_7NO. The final product is considered to be Cr_2C, CrN and C by the X-ray analysis. The thermoanalytical data for complex are given in Table 1. The sequential thermal decomposition process of the complex is shown as follow:

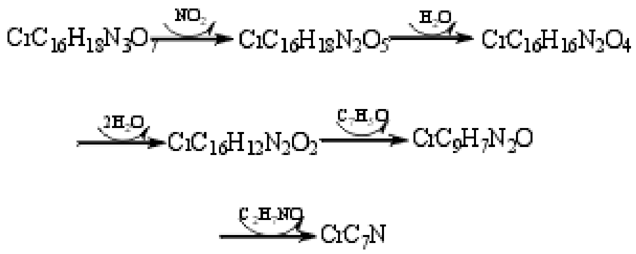

Table 1 Thermal decomposition data for $[Cr(salen)(H_2O)_2]NO_3$ complex from TG-DTG-DTA

Stage	Decomp. temp. range/°C	T_p^a/°C	Mass loss / %		Probably expelled composition
		acc. to DTG	found	calc.	
I	25–160	134.8	11.30	11.05	$-NO_2$
II	160–207	176.5	3.96	4.33	$-H_2O$
III	207–297	251.8	8.80	8.65	$-2H_2O$
IV	297–602	458.5	25.98	25.25	$-C_7H_5O$
V	602–977	823.9	14.46	14.67	$-C_2H_7NO$

[a] T_p – temperature of peak

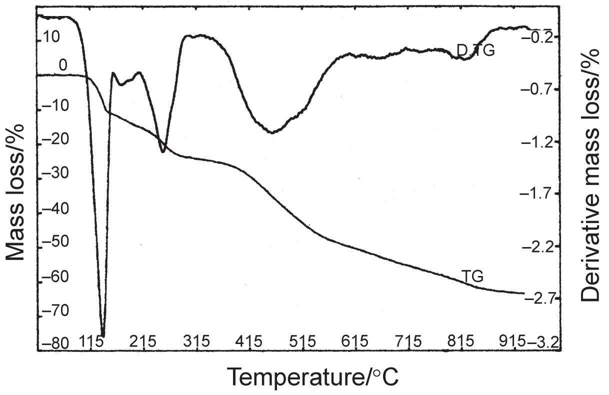

Fig. 2 TG and DTG curve of the $[Cr(salen)(H_2O)_2]NO_3$

Non-isothermal kinetic studies

For a single TG-DTG curve, the Achar differential equation [12] and the Coats–Redfern integral equation [13] are used to analyze the non-isothermal decomposition process. The integral and differential equations are as follows:

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/RT \tag{1}$$

$$\ln[g(\alpha)/T^2] = \ln(AR/\beta E) - E/RT \tag{2}$$

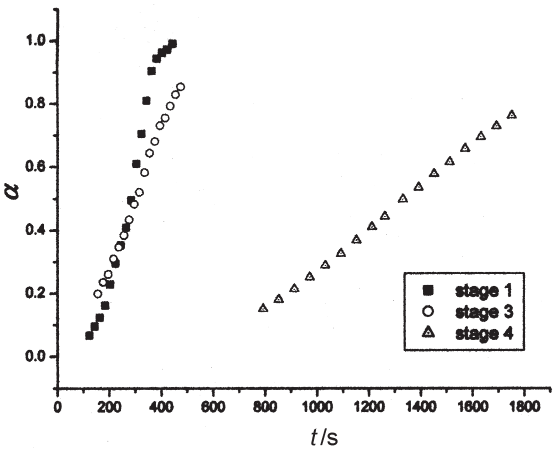

Fig. 3 Fraction decomposition α *vs.* *t* curve for non-isothermal decomposition of $[Cr(salen)(H_2O)_2]NO_3$

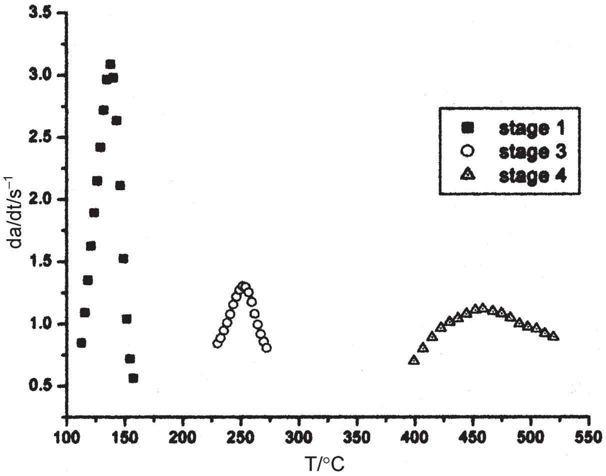

Fig. 4 dα/d*t* *vs.* *t* curve for non-isothermal decomposition of $[Cr(salen)(H_2O)_2]NO_3$

In the above equations, α – is the fractional decomposition; *T* – the absolute temperature (K); dα/d*t* – the reaction rate; *A* – the pre-exponential Arrhenius factor (S^{-1}); β – the heating rate (K min^{-1}); *E* – the apparent activation energy (J mol^{-1}); *R* – the gas constant (J mol^{-1} K^{-1}); *f*(α) and *g*(α), the differential and integral functions [14].

We studied the decomposition processes of $[Cr(salen)(H_2O)_2]NO_3$ complex for the first, the third and the fourth stage.

The basic parameters of *T*, α, and dα/d*t* were obtained from the dynamic curves of $[Cr(salen)(H_2O)_2]NO_3$ complex (shown in Figs 3–4). The basic data and kinetic model functions *f*(α) and *g*(α) were inserted into Eqs (1) and (2) respectively, and plotted

$\ln[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)]$ and $\ln[g(\alpha)/T^2]$ *vs.* $1/T$, respectively. The kinetic analysis was completed with the linear least-squares method. Comparing the kinetic parameters obtained from different methods, we selected the probable kinetic model function by which the calculated values of E and $\ln A$ were close to each other with the better linear correlation coefficient and the results were listed in Table 2. Then, it can be concluded that kinetic equation of thermal decomposition of the complex for every stage.

Table 2 Kinetic parameter for the thermal decomposition data of $[\mathrm{Cr(salen)(H_2O)_2}]\mathrm{NO_3}$

Function	Integral method			Differential method		
No.	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
7	125.31	36.20	0.9975	123.51	38.31	0.9931
6	258.64	56.60	0.9995	254.43	57.89	0.9993
6	162.20	22.25	0.9990	154.24	24.28	0.9993

Thus, the kinetic equation of the first decomposition process is as follows:

$$\mathrm{d}\alpha/\mathrm{d}t = A\mathrm{e}^{-E/RT}(1-\alpha)$$

It is seen that the first stage of decomposition for $[\mathrm{Cr(salen)(H_2O)_2}]\mathrm{NO_3}$ is controlled by random nucleation and subsequent growth mechanism. For the third stage, the kinetic equation of thermal decomposition of $[\mathrm{Cr(salen)(H_2O)_2}]\mathrm{NO_3}$ complex is:

$$\mathrm{d}\alpha/\mathrm{d}t = A\mathrm{e}^{-E/RT}\frac{3}{2}(1-\alpha)^{4/3}\left[(1-\alpha)^{-1/3}-1\right]^{-1}$$

It is seen that the third stage of decomposition for $[\mathrm{Cr(salen)(H_2O)_2}]\mathrm{NO_3}$ is controlled by three-dimensional diffusion mechanism.

The kinetic equation of thermal decomposition for the fourth stage is similar to the third decomposition process.

Conclusions

- The sinters of complex $[\mathrm{Cr(salen)(H_2O)_2}]\mathrm{NO_3}$ at the last stage is $\mathrm{Cr_2C}$, CrN and C, which are confirmed by using X-ray analysis and TG studies.
- The third and the fourth decomposition processes of complex $[\mathrm{Cr(salen)(H_2O)_2}]\mathrm{NO_3}$ are the same, which means that the two thermal decomposition processes are diffusion of three-dimension.

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