Kinetic studies on the non-isothermal decomposition of the complex of Schiff base containing S,N-Cd$_3$[CH$_3$O(O) C$_6$H$_3$CH = NNHC(S)NH$_2$]$_4$·(CH$_3$COO)$_2$·$\frac{1}{2}$ [CH$_3$S(O)CH$_3$]·2H$_2$O

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Abstract

The thermal decomposition of the complex of Schiff base containing S,N-Cd$_3$[CH$_3$O(O)C$_6$H$_3$CH = NNHC(S)NH$_2$]$_4$·(CH$_3$COO)$_2$·$\frac{1}{2}$[CH$_3$S(O)CH$_3$]·2H$_2$O and its non-isothermal kinetics have been studied by TG and DTG. The non-isothermal kinetic data were analyzed and the kinetic parameters for the first, second and third steps of the thermal decomposition were evaluated by two different methods — differential and integral methods — and tested by other methods. The most probable mechanism functions of the thermal decomposition reaction are:

$f(\alpha) = (1-\alpha)^2$	$g(\alpha) = (1-\alpha)^{-1} - 1$	(for the first step thermal decomposition reaction)
$f(\alpha) = (1-\alpha)$	$g(\alpha) = -\ln(1-\alpha)$	(for the second step thermal decomposition reaction)
$f(\alpha) = [-\ln(1-\alpha)]^{-1}$	$g(\alpha) = \alpha + (1-\alpha)$ $\ln(1-\alpha)$	(for the third step thermal decomposition reaction)

Keywords: Cadmium compound; Coupled technique; Kinetics; Non-isothermal; Schiff base complex

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1. Introduction

Complexes of some Schiff bases containing S and N are of increasing interest because they can be used in medicine [1]. In particular, the biochemical behaviour and function of cadmium(II) has a direct bearing on people's health [2, 3]. As part of a study of the relationship between the structure and properties and applications, a series of Schiff base complexes have been synthesized [4–7]. The present work reports TG and DTG studies on the kinetics and mechanism of the non-isothermal decomposition of the title complex.

2. Experimental

The complex $Cd_3[CH_3O(O)C_6H_3CH=NNHC(S)NH_2]_4 \cdot (CH_3COO)_2 \cdot \frac{1}{2}DMSO \cdot 2H_2O$ was synthesized and its structure was determined by single crystal X-ray diffraction methods according to the procedures reported in a previous work [8].

The TG and DTG curves were recorded simultaneously by a TGS-2-type thermal analyzer (Perkin–Elmer USA), the three different heating rates were 10, 15 and 20 K min^{-1} and the flow rate of N_2 gas was 40 cm^3 min^{-1}.

3. Results and discussion

TG and DTG curves of the complex are shown in Fig. 1, which shows that the complex decomposes, at the three different heating rates, in five stages. The processes are shown in Table 1.

Comparing the thermal decompositions at the three different heating rates showed that although the different heating rates made the intermediates of the thermal decomposition different at some stages, decomposition occurred in five stages and the final solid product was CdO.

Structure determination [8] showed that there were Van der Waals forces between the solvent molecule, DMSO, and the complex. The molecule of water and Ac$^-$ combined with the interior of the complex by hydrogen-bonding and ion-bonding forces, respectively. The dehydration and the loss of solvent (DMSO) took place in the first step. The loss of two acetic acid molecules and four aminos occurred in the second step. The loss of four methyls took place in the third step. Under the influence of the chelate effect it became much easier for the loss of the aminos and methyls in the outside of the chelate rings to occur. The two dioxygen bridges combining with three cadmium atoms in the inside of the chelate rings were broken in the final step leading to a residual mass corresponding to CdO, as confirmed by X-ray diffraction.

The Achar method (differential method) and Coats–Redfern method (integral method) were used to determine the most probable mechanisms of the thermal
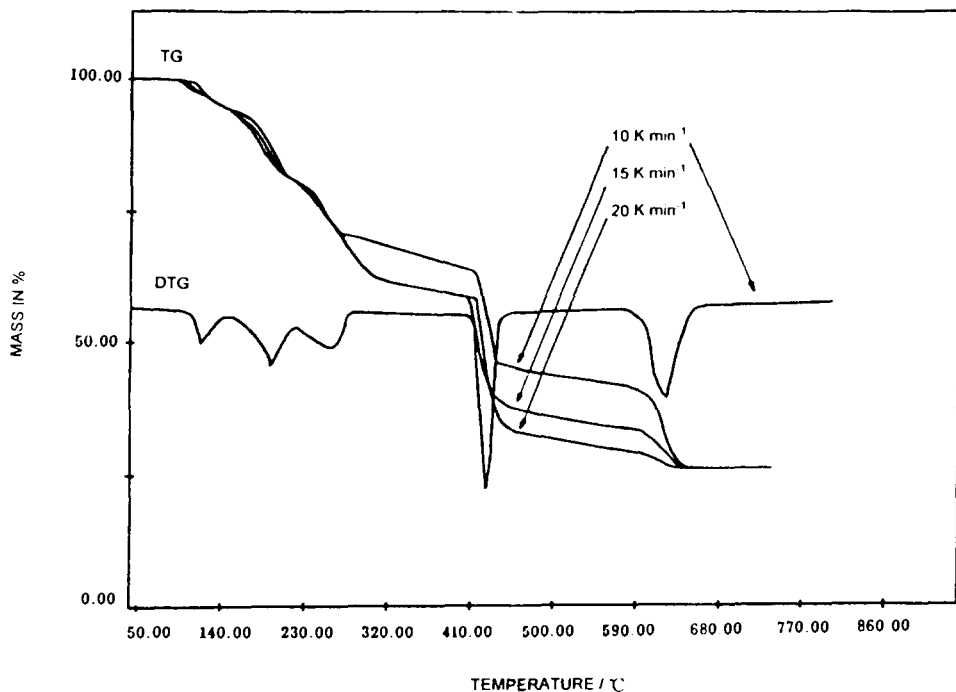
Fig. 1. The TG and DTG curves of the title complex at three heating rates.

decomposition reactions of the first, second and third steps, heating rate 10 K min^{-1}.

Achar equation [9] $\ln\left[(d\alpha/dt)/f(\alpha)\right] = \ln A - E/RT$ (1)

Coats–Redfern equation [10] $\ln\left[g(\alpha)/T^2\right] = \ln(AR/\beta E) - E/RT$ (2)

where $f(\alpha)$ and $g(\alpha)$ are the differential and integral mechanism functions, respectively α is the fractional decomposition at temperature T/K, β is the heating rate, E is the derived apparent activation energy, A is the pre-exponential factor and R is the gas constant.

The original non-isothermal kinetic data α, T and $d\alpha/dt$ for the thermal decompositions of the first, second and third steps were obtained by analyzing the TG and DTG curves. By substituting the probable mechanism functions $f(\alpha)$ and $g(\alpha)$, given in Table 2, into Eqs. (1) and (2), respectively, when plotting $\ln\left[(d\alpha/dt)/f(\alpha)\right]$, $\ln\left[g(\alpha)/T^2\right]$ against $(1/T)$, respectively, by the linear least-squares method, the values for the non-isothermal kinetic parameters E, A and the correlation coefficient, r, of the different kinetic model functions were calculated. If all conditions are in good agreement, viz. when the calculated values of E and A, obtained from a certain pair of $f(\alpha)$ and $g(\alpha)$, respectively, are closest, and the correlation coefficients r approach 1, the corresponding model function may be the mechanism function of the reaction. The important values for the non-isothermal kinetic parameters E, A and correlation coefficients r of the probable kinetic functions were listed in Table 3.

Table 1

The thermal decomposition processes of the complex $Cd_3[CH_3O(O)C_6H_3CH=NNHC(S)NH_2]_4 \cdot (CH_3COO)_2 \cdot \frac{1}{2}[CH_3S(O)CH_3] \cdot 2H_2O$ at three heating rates

Step	$\beta/K\,min^{-1}$		Intermediate	Mass loss/% [a]
1	10	50–152°C	$[Cd_3\{CH_3O(O)C_6H_3CH=NNHC(S)NH_2\}_4] \cdot (CH_3COO)_2$	5.85(5.26)
	15	50–146°C	As above	5.80(5.26)
	20	50–145°C	As above	5.80(5.26)
2	10	152–210°C	$Cd_3[CH_3O(O)C_6H_3CH=NNHC(S)]_2[CH_3O(O)C_6H_3CH=NNC(S)]_2$	12.96(12.90)
	15	146–210°C	As above	13.02(12.90)
	20	145–210°C	As above	13.02(12.90)
3	10	210–270°C	$Cd_3[O(O)C_6H_3N(S)]_2[O(O)C_6H_3CH=NNC(S)]_2$	10.59(9.82)
	15	210–320°C	$Cd_3[O(O)N(S)]_2[O(O)C_6H_3CH=NNC(S)]_2$	19.51(20.34)
	20	210–320°C	As above	19.51(20.34)
4	10	270–484°C	$Cd_3O_8N_4S_4$	26.69(26.51)
	15	320–484°C	$Cd_3O_8N_4$	25.44(24.97)
	20	320–484°C	Cd_3O_8	29.62(28.89)
5	10	484–650°C	3CdO	17.77(18.51)
	15	484–650°C	As above	10.10(9.53)
	20	484–650°C	As above	6.02(5.60)

[a] Values in parentheses are calculated values.

Table 2
Kinetic functions used for the analysis

Mechanism	Integral form g(α)	Differential form f(α)
P1 Power law	$\alpha^{1/4}$	$4\alpha^{3/4}$
	$\alpha^{1/3}$	$3\alpha^{2/3}$
	$\alpha^{1/2}$	$2\alpha^{1/2}$
	α	1
A1.5 Avrami–Erofeev	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
A2 Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
A3 Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
A4 Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
R2 Contracting surface	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
R3 Contracting volume	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
D1 1-D Diffusion	α^2	$1/2\alpha$
D2 2-D Diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	$-[\ln(1-\alpha)]^{-1}$
D3 3-D Diffusion	$[1-(1-\alpha)^{1/3}]^2$	$1.5[1-(1-\alpha)^{4/3}]^{-1}(1-\alpha)^{2/3}-1$
D4 Ginstling–Brounshtein	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
F1 First-order	$-\ln(1-\alpha)$	$1-\alpha$
F2 Second-order	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$

Table 3
Main kinetic parameters of the 1st, 2nd and 3rd steps of thermal decomposition of the title complex obtained by the differential and integral methods

	Achar method (differential form f(α))			Coats–Redfern method (integral form g(α))		
Mechanism	E/(kJ mol^{-1})	ln(A/s^{-1})	r	E/(kJ mol^{-1})	ln(A/s^{-1})	r
F2 (1st step)	145.51	49.67	0.9613	150.67	46.07	0.9762
F1 (2nd step)	115.63	32.95	0.9932	113.68	28.67	0.9996
A1.5 (2nd step)	75.18	22.18	0.9827	73.23	17.86	0.9996
D2 (3rd step)	241.67	57.69	0.9612	241.15	53.77	0.9744
D4 (3rd step)	262.21	61.11	0.9718	252.07	54.93	0.9786

(Confidence interval 95%)

From the results obtained in Table 3, the most probable mechanism function was F2 for the first step of the thermal decomposition. For further confirmation, the MacCallum–Tanner method [11] was used. According to Eq. (3)

$$\ln g(\alpha) = \ln(AE/\beta R) - 1.1 E^{0.44} - (1.0 + 0.51 E)/T \times 10^{-3} \qquad (3)$$

plotting ln g(α) against $1/T$ by the linear least-squares method gives values for E, A and r of the function F2 (list in Table 4), which combined with the results in Table 3, clearly showed that E, A values of F2 were in best fit, so this was the mechanism function for the first step of the thermal decomposition. For the second step of the thermal decomposition, the most probable mechanism function was F1, but A1.5 couldn't be excluded. From Table 3, though the calculated values of the kinetic parameter E of

Table 4
Main kinetic parameters of the 1st and 3rd steps of thermal decomposition of the title complex obtained by the MacCallum–Tanner method

Mechanism	$E/(\text{kJ mol}^{-1})$	$\ln(A/\text{s}^{-1})$	r	$E/(\text{kJ mol}^{-1})$	$\ln(A/\text{s}^{-1})$	r
	(1st Step)			(3rd Step)		
F2	146.85	49.41	0.9779	--	–	–
D2	–	–	–	238.32	57.98	0.9762
D4	--	–	–	249.35	59.21	0.9799

A1.5 were close, they were less than 80 kJ mol^{-1} [12]. On the other hand, in the thermal decomposition the broken bonds were C–N, N–H and ion-bonding. For this, the activation energy of its decomposition reaction would not be so small, so A1.5 was excluded and F1 was determined as the mechanism function for the second step of the thermal decomposition. Logically, from the results in Table 3, D2 was the most probable mechanism function for the third step of the thermal decomposition, but D4 couldn't be neglected. By the same means used for the first step, through comparison with the results in Table 4, D2 was identified as the mechanism function for the third step of the thermal decomposition.

So the mechanism functions of the thermal decomposition are:

$f(\alpha) = (1 - \alpha)^2$ $g(\alpha) = (1 - \alpha)^{-1} - 1$ (F2 for the first step)
$f(\alpha) = (1 - \alpha)$ $g(\alpha) = -\ln(1 - \alpha)$ (F1 for the second step)
$f(\alpha) = [-\ln(1 - \alpha)]^{-1}$ $g(\alpha) = \alpha + (1 - \alpha)\ln(1 - \alpha)$ (D2 for the third step)

correspondingly, their non-isothermal kinetic equations respectively are:

$d\alpha/dt = A e^{-E/RT}(1 - \alpha)^2$ (Second-order kinetics)
$d\alpha/dt = A e^{-E/RT}(1 - \alpha)$ (First-order kinetics or random nucleation and its subsequent growth; $n = 1$)
$d\alpha/dt = A e^{-E/RT}[-\ln(1 - \alpha)]^{-1}$ (Two-dimensional diffusion)

The physical meaning of the result is that in the first and second steps of the thermal decomposition, there were liquefactions and the phase boundary disappeared, but in the third step, the reaction was a diffusion-controlled reaction, there was a phase boundary which affected the reaction rate, and the reaction was the two-dimensional diffusion one which took place in a circle with a certain radius.

4. Conclusions

The thermal decompositions of the title complex, at three different heating rates, 10, 15, 20 K min^{-1} are all in five stages.

When the heating rate is 10 K min^{-1}, the most probable mechanism functions for the first, second and third steps of thermal decomposition are determined as F2, F1 and D2,

respectively. For the first step E is 145.51–150.67 kJ mol^{-1} and A is 1.02×10^{20} to 3.73×10^{21} s^{-1}. For the second step E is 113.68–115.63 kJ mol^{-1} and A is 2.83×10^{12} to 2.04×10^{14} s^{-1}. For the third step E is 238.32–241.67 kJ mol^{-1} and A is 2.25×10^{23} to 1.51×10^{25} s^{-1}.

Acknowledgements

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