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THERMAL DECOMPOSITION KINETICS OF THE Zn(II) COMPLEX WITH NORFLOXACIN IN STATIC AIR ATMOSPHERE

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Abstract

The thermal decomposition of $Zn[NFA]_2{\cdot}5H_2O$ ($NFA=C_{16}H_{18}FN_3O_3$, norfloxacin) and its kinetics were studied under non-isothermal conditions in air by TG-DTG and DTA methods. The intermediate and residue for each decomposition were identified from the TG curve. The non-isothermal kinetic data were analyzed by means of the Achar method and the Madhusudanan-Krishnan-Ninan (MKN) method. The possible reaction mechanisms were investigated by comparing the kinetic parameters. The kinetic equation for the second stage can be expressed as $d\alpha/dt=A\exp(-E/RT)(1-\alpha)$.

Keywords: non-isothermal kinetics, norfloxacin, thermal decomposition, Zn(II) complex

Introduction

Norfloxacin, a broad-spectrum antimicrobial, has been widely used in the field of clinical urethra infections, clinical enteric infections, etc. It exerts a marked curative effect [1]. In recent years, the interactions between norfloxacin and certain metal ions have been examined widely [2–5]. The fluorescence spectrum and liposolubility of the complex of Zn(II) with norfloxacin have been reported [6, 7], but its non-isothermal kinetics and thermal decomposition mechanism have been little studied. In the present paper, the thermal decomposition mechanism of the Zn(II) complex with norfloxacin is derived and the non-isothermal kinetic data are analyzed by the Achar method [8] and the MKN method [9].

Experimental

A 0.5 mol l^{-1} solution of NaOH was added to 2 mmol norfloxacin until it just dissolved. 10 ml water was added to 1 mmol $ZnCl_2$ to dissolve it, and the solution was then poured into the norfloxacin solution. The mixture was stirred and heated. The

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white solid produced was isolated by filtration, washed successively with deionized water and ethanol, and finally dried in a desiccator. Microanalyses for C, H and N were performed on an EA Heraeus model CHN-O-PAPIN elemental analyzer. The metal content was assayed by using an EDTA titration method.

All TG and DTG experiments on the title compound were performed with a Perkin Elmer TGA7 thermogravimetric analyzer. The heating rates used were 2.5, 5, 7.5 and 10°C min^{-1} from ambient to 825°C; the sample size was 1.5±0.1 mg. Air was used as a static atmosphere.

DTA curves were recorded with a Perkin Elmer DTA 1700 instrument with a system 7/4 controller, under the same conditions as in the TG analysis, except that the sample mass was 1.6 mg, the heating rate used was 5°C min^{-1} and Al_2O_3 was employed as reference material.

Results and discussion

Elemental analyses and thermogravimetric decomposition data

Analytical results on the complex and the proposed formula are given in Table 1. The experimental results coincide very well with the theoretical ones.

TG and DTG curves of the Zn(II) complex with norfloxacin at a heating rate of 5°C min^{-1} are shown in Fig. 1. The thermoanalytical data on $Zn[NFA]_2{\cdot}5H_2O$ are given in Table 2. The Zn(II) complex decomposed via intermediates to give zinc oxide as end-product. The mass loss percentages and the probable compositions of the expelled groups are also indicated in Table 2. The results of thermal analysis indicate that the Zn(II) complex with norfloxacin begins to decompose at 26°C and its de-

Table 1 Results of elemental analyses of the complex $Zn[NFA]_2{\cdot}5H_2O$ (NFA=$C_{16}H_{18}FN_3O_3$)

	Percentage of			
	C	H	N	Zn
Theoretical values	48.67	5.79	10.91	8.19
Experimental data	48.52	5.59	10.61	8.25

Table 2 Thermal decomposition data on $Zn[NFA]_2{\cdot}5H_2O$ in static air atmosphere from TG and DTG analysis

Stage	T_{range}/ °C	DTG peak temp./°C	Mass loss/%		Probable comp. of expelled group	Intermediate
			TG	theory		
I	26–144		11.08	11.37	$5H_2O$	$Zn[NFA]_2$
II	270–391	–316	54.48	54.59	NFA, C_2H_5, $2C_4H_9N_2$	$ZnC_{10}H_3FO_3N$
III	391–605	532	25.37	25.79	$C_{10}H_3FO_2N$	ZnO
			90.9[a]	91.75[a]		

[a] Total mass loss (%)

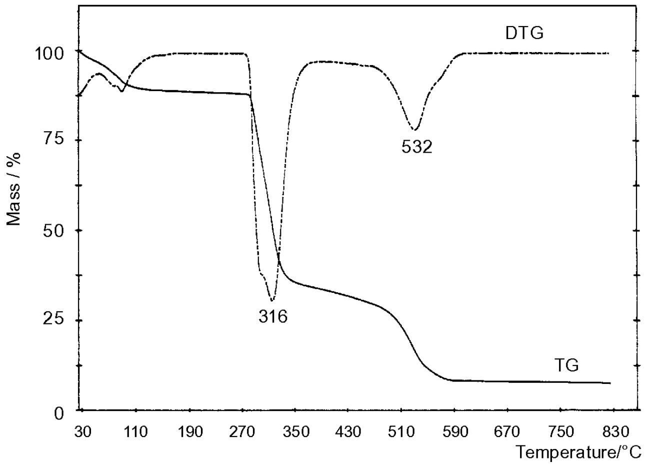

Fig. 1 TG and DTG curves of Zn[NFA]$_2$·5H$_2$O at a heating rate of 5°C min^{-1}

composition ends at 605°C. The TG curve of Zn[NFA]$_2$·5H$_2$O reveals a three-stage decomposition process, as predicted by the DTG curve (Fig. 1). The first stage is in the temperature range 26–144°C, with a mass loss of 11.08%, which corresponds to the loss of 5 mol H_2O (theoretical loss 11.37%). Actually, this stage of dehydration and decomposition involves several steps. The second stage of degradation occurs in the range 270–391°C, with a mass loss of 54.48%, in which 1 NFA, C_2H_5 and $C_4H_9N_2$ are removed, with a theoretical loss of 54.59%. This degradation was followed by the third stage of decomposition in the temperature range 391–605°C, in which $C_{10}H_3FO_2N$ was removed, with a mass loss of 25.37% (theoretical loss 25.79%). At this point, the Zn(II) complex with norfloxacin was completely degraded into ZnO, with a total loss of 90.9% (theoretical loss 91.75%). The results indicate that the thermal decomposition of the Zn(II) complex with norfloxacin can be described as

$$\mathrm{Zn[NFA]_2{\cdot}5H_2O \rightarrow Zn[NFA]_2 \rightarrow ZnC_{10}FO_3N \rightarrow ZnO}$$

DTA analysis

The DTA curve recorded between 25 and 825°C at a heating rate of 5°C min^{-1} on a sample of the title compound is given in Fig. 2. The DTA data for the complex are listed in Table 3. One endothermic peak and four exothermic peaks are apparent. The first peak (endothermic) lies between 130 and 153°C. Three exothermic peaks are found between 240 and 465°C, representing the loss of one molecule of NFA, one C_2H_5 and one $C_4H_9N_2$ from the Zn[NFA]$_2$. The fourth strong exotherm, which represents the loss of one molecule of $C_{10}H_3FO_2N$ from $ZnC_{10}H_3FO_3N$ to yield ZnO, is observed between 465 and 550°C.

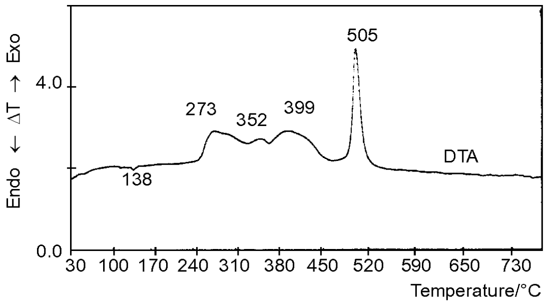

Fig. 2 DTA curve of $Zn[NFA]_2{\cdot}5H_2O$ at a heating rate of 5°C min^{-1}

Table 3 DTA temperatures for thermal decomposition of the complex in static air atmosphere

Stage	DTA temperatures[b]/°C		
	T_i	T_p	T_f
I	130	138 endo	153
II	240	273 exo	330
III	336	352 exo	365
IV	365	399 exo	465
V	465	505 exo	550

[b] T_i – initial temperature; T_p – peak temperature; T_f – final temperature

Kinetic studies of non-isothermal decomposition

In the present work, both the Achar and the MKN methods have been applied to study the kinetics of the second decomposition processes of $Zn[NFA]_2{\cdot}5H_2O$. The differential and integral equations are as follows:

$$\ln\left[\frac{\frac{d\alpha}{dt}}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \qquad \left(\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT}\right) \tag{1}$$

$$\ln\left[\frac{g(\alpha)}{T^{1.9215}}\right] = \ln A\frac{E}{\beta R} + 3.7721 - 1.9215\ln E - 0.12039\frac{E}{T} \tag{2}$$

where α is the fraction of conversion, $d\alpha/dt$ is the rate of conversion, T is the absolute teperature, A is the pre-exponential factor, R is the gas constant, E is the apparent activation energy, β is the linear heating rate, and $f(\alpha)$ and $g(\alpha)$ are the differential and integral mechanism functions, respectively. The entropy of activation (ΔS) and the free energy of activation (ΔG) can be calculated by using the following equations [10, 11]:

$$A = k\frac{T_s}{h}\exp\left(\frac{\Delta S}{R}\right) \tag{3}$$

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{4}$$

$$k(T) = \nu\exp\left(\frac{-\Delta G}{RT}\right) \tag{5}$$

where k is the Boltzmann constant, T_s is the peak temperature, h is the Planck constant, $k(T)$ is the rate constant as a function of temperature, and ν is the Einstein vibration frequency.

All the computational work was done on an IBM computer with a BASIC program. The basic parameters α, T and $d\alpha/dT$ obtained from the TG-DTG curves are listed in Table 4. The algebraic expressions of $g(\alpha)$ and $f(\alpha)$ [12, 13] for the most common mechanisms used in the kinetics of solid-state decompositions tested in this work are listed in Table 5.

Table 4 Basic data for Zn[NFA]$_2$·5H$_2$O, determined by TG and DTG

No.	Stage II		
	T	α	$d\alpha/dT$
1	566.88	0.2209	4.485
2	569.38	0.2765	4.875
3	571.88	0.3265	4.972
4	574.38	0.3727	5.003
5	576.88	0.4194	5.059
6	579.38	0.4678	5.161
7	581.88	0.5185	5.292
8	584.38	0.5707	5.426
9	586.88	0.6233	5.522
10	589.38	0.6757	5.558
11	591.85	0.7265	5.502
12	594.40	0.7728	5.325
13	596.89	0.8141	5.012

On substitution of the basic parameters in Table 4 and the 32 different mechanism functions $f(\alpha)$ and $g(\alpha)$ in Table 5 into Eqs (1) and (2), the kinetic parameters E and A and the linear correlation coefficients r in Table 6 were obtained with the linear least squares method. When the values of E and $\ln A$ obtained by the two methods are approximately equal, the linear correlation coefficient is better and the values of E and $\ln A$ accord with the universal law (the value of E ranges from 80 to

Table 5 Kinetic functions of $f(\alpha)$ and $g(\alpha)$ used for the present analysis

Function no.	Name of the function	$g(\alpha)$	$f(\alpha)$	Mechanism
1	Parabola law	α^2	$1/(2\alpha)$	One-dimensional, 1D
2	Valensi equation	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$	Two-dimensional, 2D
3	Ginstling-Brounstein equation	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	Three-dimensional, 3D cylindrical symmetry
4	Jander equation	$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	Three-dimensional, 3D spherical symmetry
5	Anti-Jander equation	$[(1+\alpha)^{1/3}-1]^2$	$3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	Three-dimensional, 3D
6	Zhuralev, Lesokin and Tempelman equation	$[\{1/(1-\alpha)\}^{1/3}-1]^2$	$3/2(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$	Three-dimensional, 3D
7	Avrami-Erofeev equation	$-\ln(1-\alpha)$	$(1-\alpha)$	Assumed random nucleation and its subsequent growth, $n=1$
8	Avrami-Erofeev equation	$[-\ln(1-\alpha)]^{2/3}$	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	Assumed random nucleation and its subsequent growth, $n=1.5$
9	Avrami-Erofeev equation	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	Assumed random nucleation and its subsequent growth, $n=2$
10	Avrami-Erofeev equation	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	Assumed random nucleation and its subsequent growth, $n=3$
11	Avrami-Erofeev equation	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	Assumed random nucleation and its subsequent growth, $n=4$
12		$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	Contracting sphere (cylindrical symmetry)
13		$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	Contracting sphere (spherical symmetry)

Table 5 Continued

Function no.	Name of the function	$g(\alpha)$	$f(\alpha)$	Mechanism
14	Mampel power law	α	1	Chemical reaction
15	Mampel power law	$\alpha^{1/2}$	$2\alpha^{1/2}$	
16	Mampel power law	$\alpha^{1/3}$	$3\alpha^{2/3}$	
17	Mampel power law	$\alpha^{1/4}$	$4\alpha^{3/4}$	
18	Second order	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$	Chemical reaction
19		$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$	Chemical reaction
20		$\alpha^{2/3}$	$2/3\alpha^{-1/2}$	
21	Exponential law	$\ln\alpha$	α	
22	Prout-Tomkins	$\ln[\alpha/(1-\alpha)]$	$\alpha(1-\alpha)$	Branching nuclei
23		$[-\ln(1-\alpha)]^2$	$1/2(1-\alpha)[-\ln(1-\alpha)]^{-1}$	
24		$[-\ln(1-\alpha)]^3$	$1/3(1-\alpha)[-\ln(1-\alpha)]^{-2}$	
25		$[-\ln(1-\alpha)]^4$	$1/4(1-\alpha)[-\ln(1-\alpha)]^{-3}$	
26	Third order	$[1/(1-\alpha)]^2$	$1/2(1-\alpha)^3$	
27		$1-(1-\alpha)^{1/4}$	$4(1-\alpha)^{3/4}$	
28		$1-(1-\alpha)^2$	$1/2(1-\alpha)^{-1}$	
29		$1-(1-\alpha)^3$	$1/3(1-\alpha)^{-2}$	
30		$1-(1-\alpha)^4$	$1/4(1-\alpha)^{-3}$	
31		$[1-(1-\alpha)^{1/3}]^{1/2}$	$6[1-(1-\alpha)^{1/3}]^{1/2}(1-\alpha)^{2/3}$	
32		$[1-(1-\alpha)^{1/2}]^{1/2}$	$4\{(1-\alpha)[1-(1-\alpha)^{1/2}\}^{1/2}$	

Table 6 Kinetic parameters for the thermal decomposition data of Zn[NFA]$_2$·5H$_2$O; stage II

Function no.	Achar method					MKN method				
	E/ kJ mol^{-1}	ln$A$/ s^{-1}	r	ΔS/ J mol^{-1}	ΔG/ kJ mol^{-1}	E/ kJ mol^{-1}	ln$A$/ s^{-1}	r	ΔS/ J mol^{-1}	ΔG/ kJ mol^{-1}
1	130.2	30.06	0.9739	–0.6723	130.6	225.4	44.16	0.9853	116.6	156.7
2	185.5	41.19	0.9930	91.85	131.4	256.5	50.24	0.9906	167.1	158.0
3	208.2	44.52	0.9963	119.5	137.8	269.2	51.49	0.9923	177.5	164.5
4	251.5	53.74	0.9988	196.2	135.8	295.0	57.09	0.9951	224.1	162.9
5	91.91	19.53	0.9542	–88.19	143.9	198.4	35.98	0.9820	48.53	169.8
6	381.2	81.39	0.9980	426.1	130.1	381.5	75.76	0.9986	379.3	157.9
7	142.6	33.49	0.9929	27.84	126.2	163.4	32.15	0.9977	16.76	153.6
8	85.04	21.29	0.9740	–73.54	128.4	105.8	19.95	0.9971	–84.70	155.7
9	56.26	15.11	0.9355	–124.9	129.9	77.05	13.76	0.9970	–136.1	157.2
10	27.49	8.817	0.7699	–177.3	132.0	48.32	7.462	0.9975	–188.5	159.4
11	13.10	5.582	0.4855	–204.2	133.4	33.87	4.175	0.9965	–215.9	161.1
12	77.72	18.96	0.9965	–92.91	132.5	133.4	24.86	0.9926	–43.92	159.2
13	99.35	23.17	0.9956	–57.95	133.5	142.9	26.55	0.9949	–29.82	160.5
14	12.84	5.830	0.7273	–202.1	132.0	108.1	19.95	0.9841	–84.74	158.0
15	–45.82	–6.630	0.9890	–305.7	134.4	49.37	7.452	0.9807	–188.6	160.5
16	–65.38	–10.96	0.9936	–341.7	136.0	29.83	3.068	0.9768	–225.1	162.5

Table 6 Continued

Function no.	Achar method					MKN method				
	E/ kJ mol^{-1}	ln$A$/ s^{-1}	r	ΔS/ J mol^{-1}	ΔG/ kJ mol^{-1}	E/ kJ mol^{-1}	ln$A$/ s^{-1}	r	ΔS/ J mol^{-1}	ΔG/ kJ mol^{-1}
17	–75.16	–13.21	0.9945	–360.4	137.3	20.04	0.7368	0.9688	–244.5	164.1
18	272.4	61.14	0.9876	257.8	120.4	237.8	48.33	0.9987	151.2	148.7
19	207.5	46.62	0.9896	137.0	126.7	55.55	9.613	0.9719	–170.7	156.1
20	71.50	18.00	0.9597	–100.9	131.0	68.91	11.68	0.9823	–153.5	159.4
21	–104.5	–17.71	0.9939	–397.8	130.0	–190.1	–40.96	0.9941	591.1	158.2
22	25.27	9.949	0.5852	–167.9	124.2	25.10	1.537	0.0096	–237.8	165.2
23	315.3	69.54	0.9997	327.6	122.2	336.1	68.17	0.9976	316.2	149.7
24	488.0	105.3	0.9993	624.9	119.3	508.8	103.9	0.9976	613.3	147.3
25	660.6	140.9	0.9991	921.3	117.3	681.4	139.5	0.9976	909.5	145.4
26	402.1	89.49	0.9853	493.4	111.3	250.2	52.47	0.9779	185.8	140.7
27	110.2	25.19	0.9949	–41.19	134.4	147.8	27.34	0.9955	–23.29	161.5
28	56.09	15.05	0.9940	–125.5	130.0	142.8	27.64	0.9946	–20.82	155.1
29	77.72	19.66	0.9964	–87.15	129.1	133.3	25.55	0.9926	–38.15	155.8
30	99.34	24.27	0.9956	–48.83	128.1	124.4	23.59	0.9905	–54.49	156.6
31	23.28	7.537	0.8436	–187.9	134.0	66.74	10.89	0.9932	–160.0	161.0
32	48.38	12.39	0.9821	–147.6	135.4	62.03	10.02	0.9912	–167.2	160.6

250 kJ mol^{-1} and ln$A$ from 16.91 to 69.09 s^{-1}) [14]. It can then be concluded that the relevant function is the probable thermal decomposition mechanism of the complex.

For the second stage of decomposition of the title compound, it can be suggested that the function of the possible mechanism is function no. 7 in Table 5, based on the data in Table 6. Therefore, the second stage of the decomposition mechanism is controlled by assumed random nucleation and its subsequent growth (n=1, Avrami-Erofeev equation). The kinetic equation of this process is $d\alpha/dt=A\exp(-E/RT)(1-\alpha)$. Further, in order to assess the values of the most probable mechanism obtained in the present study, the Ozawa [15] method was used to calculate the activation energy of the second decomposition step (E=150.9 kJ mol^{-1}, r=0.9986). We found that the E and r values are close to the average value given by the differential and integral methods.

Conclusions

The thermal decomposition of $Zn[NFA]_2\cdot 5H_2O$ occurs in three steps. The elimination of water takes place at temperatures below 144°C. The second step of the decomposition mechanism is controlled by assumed random nucleation and its subsequent growth (n=1, Avrami-Erofeev equation). The kinetic equation of this process is $d\alpha/dt=A\exp(-E/RT)(1-\alpha)$. In the second stage, the activation energy is 153.0 kJ mol^{-1}, the entropy of activation (ΔS) is 22.29 J mol^{-1}, and the free energy of activation (ΔG) is 139.9 kJ mol^{-1}.

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