

NON-ISOTHERMAL KINETIC STUDY OF THE DECOMPOSITION OF SOME Fe^{III} AND Cu^{II} COORDINATION COMPOUNDS

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ABSTRACT

This paper contains the non-isothermal kinetic analyses of ten solid–gas thermal decompositions. The values of the kinetic parameters estimated by using two groups of methods show a satisfactory agreement.

INTRODUCTION

In some previous notes we developed several methods for non-isothermal kinetic analysis [1–3]. This paper aims to check their validity on the non-isothermal kinetic analysis of the decomposition reactions of some coordination compounds.

EXPERIMENTAL

The following coordination compounds were used: $\text{NH}_4[\text{Fe}_2(\text{HCOO})_7] \cdot \text{H}_2\text{O}$ (S_1); $(\text{NH}_4)_3[\text{CuFe}(\text{C}_2\text{O}_4)\text{Cl}_2(\text{OH})_4]$ (S_2); $(\text{NH}_4)_3[\text{CuFe}_3(\text{HCOO})_9\text{Cl}_5(\text{H}_2\text{O})_6]$ (S_3).

The three compounds S_1 , S_2 and S_3 were synthesised according to methods described elsewhere [4]. The thermal decomposition curves were recorded

with a Paulik–Paulik–Erdey type derivatograph (MOM, Budapest) with various heating rates between 2.5 and 10 K min⁻¹. To accommodate the limitation of lack of mass transfer, small amounts of powder (up to 0.1 g) were used.

The X-ray powder diffractograms were recorded with a Philips diffractometer (P.W. 1140/90) using chromium K_α radiation.

In Table 1 the Bragg angle, θ , interplanar distances, d , relative intensities of the line, i_r , and mean crystallite sizes, r , calculated according to Scherrer's formula are given [5].

The kinetic parameters of the decomposition were obtained by using:

- (a) the method of integration over small temperature intervals, M_I [1],
- (b) the method of integration over small temperature intervals, M_{II} [2],
- (c) the improved Coats–Redfern method, M_{III} [3].

To check the accuracy of these methods, developed by two of the present authors, the non-isothermal kinetic parameters were alternatively evaluated with the methods of Coats–Redfern, M_I [6], Freeman–Carroll, M_2 [7], and Achar–Brindley–Sharp, M_3 [8].

RESULTS AND DISCUSSION

Decomposition of S_1

According to thermogravimetric data the decomposition of S_1 exhibits the

TABLE 1
Preliminary X-ray diffraction data concerning the coordination compounds S_1 – S_3

Compound S_1							
θ	10°24'	18°25'	21°18'	23°24'			
d (Å)	6.329	3.612	3.223	2.877			
i_r (%)	100	3.8	33	21			
r (µm)	0.051	–	–	–			
Compound S_2							
θ	11°39'	13°36'	16°48'	17°42'	24°30'		
d (Å)	5.652	4.859	3.953	3.758	2.755		
i_r (%)	43	38	19	31	100		
r (µm)	–	–	–	–	0.061		
Compound S_3							
θ	10°42'	12°	18°24'	18°36'	21°30'	23°36'	24°36'
d (Å)	6.154	5.496	3.620	3.582	3.118	2.854	2.745
i_r (%)	100	53	28	28	32	33	32
r (µm)	0.054	–	–	–	–	–	–

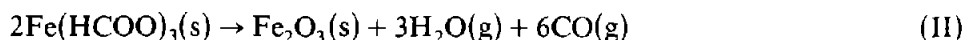
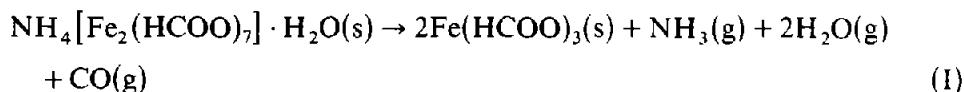
TABLE 2

Thermogravimetric data for reactions I and II

<i>Reaction I</i>									
<i>T</i> (K)	333	343	353	363	373	383	393	403	413
α^a	0.094	0.153	0.241	0.341	0.471	0.606	0.753	0.859	0.888
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	5.3	7.4	9.4	11.5	13.3	14.1	12.7	6.8	5.0
<i>Reaction II</i>									
<i>T</i> (K)	433	443	453	463	473	483	493	503	
α^a	0.019	0.046	0.081	0.143	0.243	0.370	0.576	0.957	
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	2.3	3.1	4.9	8.1	11.4	16.7	29.4	22.5	

^a Conversion degree.

following steps



The TG, DTG and *T* data, worked in terms of the conversion, are given in Table 2.

The non-isothermal kinetic parameters for reactions I and II are given in Table 3.

An inspection of the results given in Table 3 shows a satisfactory agreement between the values of the non-isothermal kinetic parameters obtained by our methods and those obtained by other methods given in the literature.

TABLE 3

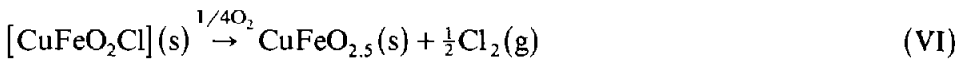
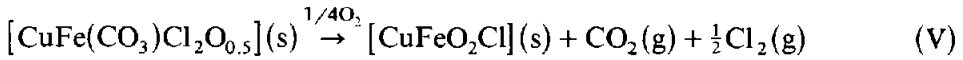
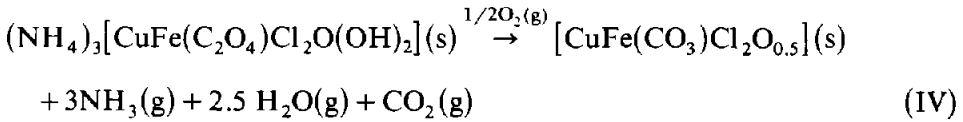
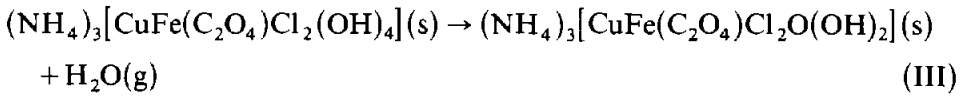
Non-isothermal kinetic parameters of reactions I and II

Method	<i>n</i> ^a	<i>A</i> (s ⁻¹)	<i>E</i> (kcal mol ⁻¹)
<i>Reaction I</i>			
<i>M</i> _{II}	1	5.5 × 10 ³	10.4
<i>M</i> _{III}	1	2.4 × 10 ³	9.8
<i>M</i> ₁	1	3.3 × 10 ³	10.1
<i>M</i> ₃	1	1.6 × 10 ³	9.5
<i>Reaction II</i>			
<i>M</i> _{II}	0	1.5 × 10 ⁷	21.4
<i>M</i> _{III}	0	1.2 × 10 ⁷	21.2
<i>M</i> ₁	0	6.3 × 10 ⁶	20.7
<i>M</i> ₃	0	2.8 × 10 ⁶	19.9

^a Reaction order.

Decomposition of S_2

The TG curves exhibit the following decomposition steps which occur by heating the samples from room temperature to 600°C.



The thermogravimetric data and the values of the non-isothermal kinetic parameters of reactions III–VI are given in Tables 4 and 5, respectively.

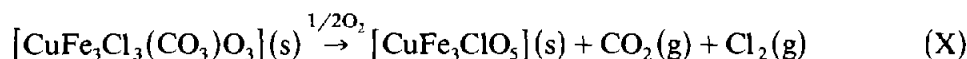
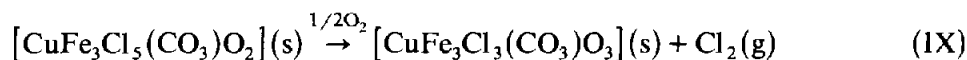
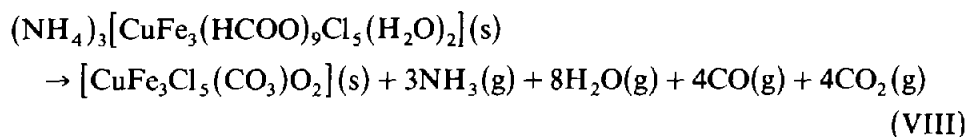
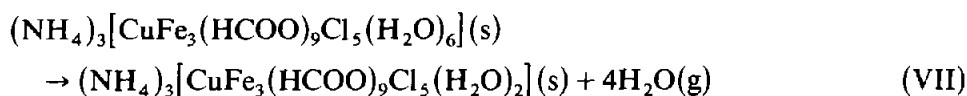
These results also show for reactions III–VI a quite satisfactory agreement between the non-isothermal kinetic parameter values obtained by various methods.

TABLE 4
Thermogravimetric data for reactions III–VI

<i>Reaction III</i>								
<i>T</i> (K)	303	313	323	333	343	353	363	373
α	0.06	0.14	0.24	0.36	0.52	0.66	0.82	0.92
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	6	9	11	14	15	15	13	8
<i>Reaction IV</i>								
<i>T</i> (K)	438	448	458	468	478	488	498	
α	0.031	0.079	0.157	0.317	0.561	0.861	0.999	
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	4	6.3	11.4	20.4	27.7	31.4	14.1	
<i>Reaction V</i>								
<i>T</i> (K)	523	533	543	553	563	573	583	
α	0.101	0.169	0.278	0.435	0.634	0.851	0.981	
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	5.5	8.9	13.3	17.8	20.8	17.3	7.5	
<i>Reaction VI</i>								
<i>T</i> (K)	663	683	703	723	743	763	783	
α	0.061	0.146	0.272	0.473	0.708	0.902	0.998	
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	3.1	5.2	8.5	11.4	11.1	6.1	4.5	

Decomposition of S_3

The thermogravimetric data show the following decomposition steps of the binuclear coordination compound S_3



The thermogravimetric data and the values of the non-isothermal kinetic parameters for reactions VII–X are given in Tables 6 and 7, respectively.

TABLE 5

Non-isothermal kinetic parameters of reactions III–VI

Method	n	A (s^{-1})	E (kcal mol^{-1})
<i>Reaction III</i>			
M_{II}	1.0	2.7×10^3	8.9
M_{III}	1.0	1.1×10^4	9.8
M_1	1.0	1.5×10^4	10.1
M_2	1.1	3.8×10^4	9.2
<i>Reaction IV</i>			
M_1	0.61	1.5×10^{10}	26.8
M_{II}	0.66	2.5×10^{11}	29.4
M_{III}	0.66	1.1×10^{11}	28.7
M_1	0.66	1.4×10^{11}	28.9
M_2	0.60	1.0×10^{11}	28.5
<i>Reaction V</i>			
M_1	0.70	2.4×10^9	29.6
M_{II}	0.66	8.5×10^8	28.8
M_{III}	0.66	2.3×10^9	29.7
M_1	0.66	1.2×10^9	28.9
M_2	0.72	1.3×10^9	29.1
<i>Reaction VII</i>			
M_{II}	1	1.2×10^7	31.4
M_{III}	1	3.3×10^7	32.9
M_1	1	1.8×10^7	32.2
M_2	0.95	5.5×10^7	33.7

TABLE 6

Thermogravimetric data for reactions VIII-X

<i>Reaction VII</i>								
<i>T</i> (K)	353	363	373	383	393	403	413	423
α	0.12	0.189	0.303	0.432	0.591	0.727	0.833	0.924
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	7.2	9.1	12.2	14.7	15.3	12.1	9.7	8.4
<i>Reaction VIII</i>								
<i>T</i> (K)	453	463	473	483	493	503	513	
α	0.047	0.112	0.253	0.453	0.694	0.859	0.970	
$\frac{d\alpha}{dt} \times 10^3$ (K ⁻¹)	4.7	10.3	17.1	22.1	20.3	13.8	7.1	
<i>Reaction IX</i>								
<i>T</i> (K)	523	533	543	553	563	573	583	
α	0.129	0.201	0.297	0.543	0.627	0.801	0.978	
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	6	8.4	12.1	16.5	17.9	17.6	10.1	
<i>Reaction X</i>								
<i>T</i> (K)	673	683	693	703	713	723	733	743
α	0.101	0.153	0.222	0.323	0.443	0.591	0.755	0.901
$\frac{d\alpha}{dT} \times 10^3$ (K ⁻¹)	4.3	6.1	8.5	11.1	13.4	15.6	15.4	11.5

TABLE 7

Non-isothermal kinetic parameters of reactions VII-X

Method	<i>n</i>	<i>A</i> (s ⁻¹)	<i>E</i> (kcal mol ⁻¹)
<i>Reaction VII</i>			
<i>M</i> _I	0.96	1.5 × 10 ³	9.8
<i>M</i> _{III}	1.00	3.4 × 10 ⁴	12.1
<i>M</i> ₁	1.00	1.9 × 10 ⁴	11.7
<i>M</i> ₂	0.97	5.7 × 10 ³	10.7
<i>Reaction VIII</i>			
<i>M</i> _I	1.1	5.4 × 10 ¹⁰	28.4
<i>M</i> _{II}	1.0	7.7 × 10 ¹⁰	28.8
<i>M</i> _{III}	1.0	2.8 × 10 ¹¹	30.1
<i>M</i> ₁	1.0	1.1 × 10 ¹¹	29.4
<i>Reaction IX</i>			
<i>M</i> _{II}	0.50	8.1 × 10 ⁶	23.7
<i>M</i> _{III}	0.50	6.6 × 10 ⁵	23.5
<i>M</i> ₁	0.50	9.4 × 10 ⁶	23.9
<i>M</i> ₂	0.57	1.4 × 10 ⁷	24.3
<i>Reaction X</i>			
<i>M</i> _I	0.60	1.4 × 10 ⁷	31.3
<i>M</i> _{II}	0.66	8.3 × 10 ⁷	34.3
<i>M</i> _{III}	0.66	4.4 × 10 ⁸	36.8
<i>M</i> ₁	0.66	2.4 × 10 ⁸	35.8
<i>M</i> ₂	0.66	6.8 × 10 ⁷	33.7

For reactions VII–X a quite satisfactory agreement between the values of the non-isothermal kinetic parameters evaluated by various methods can also be noted.

The subunitary values of the reaction order 0, 1/2, 2/3 came from the general rate equation

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (1)$$

with $m = 0$. These values indicate either physical phenomena which are rate limiting ($n = 0$), or surface-controlled reactions ($n = 1/2, 2/3$) [9,10]. The values of n close to unity could be assigned to a chemical reaction limited decomposition (for A values close to 5×10^{12} as predicted by the transition state theory [11]). This is perhaps the case for reaction VIII.

As far as reactions I, III, VI and VII are concerned, the first-order kinetic equation which formally describes the decomposition should be treated as a particular form of Avrami–Erofeev [12,13] equation

$$\ln(1/1 - \alpha) = kt^p \quad (2)$$

for $p = 1$.

CONCLUSIONS

The non-isothermal kinetic parameters of ten solid–gas decompositions have been evaluated by using newly worked methods and methods already known in the literature. A satisfactory agreement of the non-isothermal kinetic parameters obtained by the two groups of methods has been noted.

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