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THERMAL DECOMPOSITION KINETICS OF SOLID IRON(III) TRIS-*N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE

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ABSTRACT

The thermal decomposition kinetics of solid iron(III) tris-*N*-benzoyl-*N*-phenylhydroxylamine have been studied by the isothermal heating technique. The iron complex decomposes in the range 160–172°C, according to a model based on liquid phase formation. Other kinetics models which should account for the experimental evidence are discussed.

INTRODUCTION

The kinetics of solid thermal decomposition reactions are interpreted in terms of nucleus formation and growth from original solid matrix products [1–4]. The kinetic equations usually used in the study of solid thermolysis can be classified into three groups [2,3], according to the prevailing reaction mechanism: diffusion-controlled processes (D), limitrophe phase reaction-controlled processes (R) and nuclear-growth-controlled processes (A). Machado et al. [5] have studied the thermal decomposition of complexes formed between the *N*-benzoyl-*N*-phenylhydroxylamine ligand and the Cr^{3+} ion ($Cr(BPHA)_3$) and have observed that three different mechanisms could describe the decomposition kinetics: the Avrami–Erofeev law, with $m = 4$, and two other mechanisms not usually employed in solid thermolysis, in which the principal decomposition product, the benzanilide, plays an important role. In the present work, we have studied the $Fe(BPHA)_3$ thermal decomposition with the objective of gaining a better knowledge of the decomposition kinetics of chelates of the type $M(BPHA)_3$, where $M \equiv$ trivalent metals. It was observed that only one of the models proposed by Machado and collaborators [5] was compatible with the experimental data.

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EXPERIMENTAL

$Fe(BPHA)_3$ was synthesised according to the method described by Chan and Moshier [6] and purified by chromatography through a cellulose column, using a benzene/cyclohexane mixture (70/30 vol.%) as eluent. After the solvent was evaporated, the complex was vacuum-dried overnight and ground to pass 300 mesh. Elemental analysis for $Fe(C_{13}H_{10}O_2N_3$ (wt.%) was: calculated, Fe = 8.06, C = 67.64, H = 4.37, N = 6.07 and O = 13.86; found, Fe = 7.88, C = 67.40, H = 4.36, N = 5.98 and O = 13.78.

The thermal decomposition experiments were carried out using an oil bath (Herbruder Haake, Berlin) with a thermal stability within $\pm 0.2\,^\circ$C. The samples ($\approx$ 15 mg) were introduced into thin-walled Pyrex tubes 10 cm long and of diameter 0.5 cm which were immersed in the oil bath. After heating, the tubes were rapidly cooled down to room temperature before analysis, by immersing them in water. The undecomposed fractions $(1-\alpha)$ were separated in a chromatographic column with the same experimental conditions as described above for the purification process. The eluted solutions were collected in 25 cm^3 volumetric flasks and the volume made up with the solvent-mixture eluent. The undecomposed fractions were determined by spectrophotometric procedure (PMQ-II, Carl Zeiss spectrophotometer) using the absorption band in the visible region with $\lambda_{max} = 440$ nm and $\epsilon_{max} = (4.58 \pm 0.08) \times 10^3$ l mol^{-1} cm^{-1}.

RESULTS AND DISCUSSION

A series of isothermal experiments was run in the temperature range 160.0–172.0 °C. The plots of decomposed fraction α against t display the well-known sigmoid shape characteristic of many solid state thermal decompositions [7]. The curves of the reaction rate $d\alpha/dt$ plotted as a function of α have the shape shown in Fig. 1.

The reaction rate increases gradually as α increases, reaching a maximum near $\alpha = 0.70$, and then decreases to approximately zero values at $\alpha > 0.90$. Table 1 displays the α_{max} values obtained for the different temperatures studied. It may be seen that α_{max} is temperature independent and possesses a mean value of 0.73 ± 0.03. Table 2 summarises the principal kinetic models used in the studies of solid thermal decomposition, showing the α_{max} value for each one. The symbols used are the same as are usually found in the literature [2,3,8], except where otherwise indicated. From the plots, it follows that only the A_m, A_n and A_x equations suggest α_{max} values different from zero or 1. However, none of these explains the α_{max} value of 0.73 observed for $Fe(BPHA)_3$. On the other hand, an attempt to fit the experimental data to these three theoretical models gave no satisfactory results, as

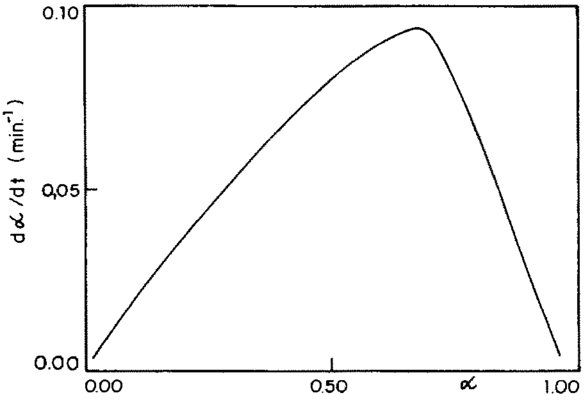

Fig. 1. Typical $d\alpha/dt$ vs. α plots for $Fe(BPHA)_3$.

TABLE 1

α_{max} values for the decomposition of $Fe(BPHA)_3$

T(°C)	160.0	162.6	164.2	166.2	168.0	170.0	172.0
α_{max}	–	0.77	0.71	0.76	0.69	0.69	0.73

TABLE 2

Kinetic equations for the solid thermal-decomposition reactions

Rate-controlling processes	Symbols [a]	Equations	α_{max}
Diffusion	D_1	$\alpha^2 = kt$	0
	D_2	$(1-\alpha)\ln(1-\alpha)+\alpha = kt$	0
	D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	0
	D_4	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	0
Phase boundary reaction	R_1	$1-(1-\alpha) = kt$	0
	R_2	$1-(1-\alpha)^{1/2} = kt$	0
	R_3	$1-(1-\alpha)^{1/3} = kt$	0
Nucleation and nuclei growth	A_m	$[-\ln(1-\alpha)]^{1/m} = kt$	
		$m = 2, 3, 4, \ldots$	$1-\exp[(1-m)/m]$
	A_n	$\ln[\alpha/(1-\alpha)] = kt + C$,	
		$k > 1$	0.5
	A_x	$\ln[\alpha/(1-\alpha)] = k \ln t + C$,	
		$k > 1$	$0.5-1/(2k)$
	P_n	$\alpha^{1/n} = kt$	1
	F_1	$-\ln(1-\alpha) = kt$	0

[a] Symbols used by the authors.

TABLE 3

Linear correlation coefficients to fit the equations (1), (2) and (3) to the experimental data for $Fe(BPHA)_3$ thermolysis

T (°C)	160.0	162.6	164.2	166.2	168.0	170.0	172.0
Eqn. (1)	0.947	0.962	0.962	0.967	0.956	0.953	0.969
Eqn. (2)	0.997	0.783	0.875	0.896	0.835	0.918	0.854
Eqn. (3)	0.993	0.896	0.947	0.955	0.930	0.963	0.924

shown in Table 3. In fact, for the Prout–Tompkins equation [9,10], $\ln[\alpha/(1-\alpha)]$ must be a linear function of t or $\ln t$, according to the expressions

$$\ln[\alpha/(1-\alpha)] = kt + C \tag{1}$$

or

$$\ln[\alpha/(1-\alpha)] = k \ln t + C \tag{2}$$

In the case of the Avrami–Erofeev equation [11,12], the term $\ln[-\ln(1-\alpha)]$ is a linear function of $\ln t$, according to the expression

$$\ln[-\ln(1-\alpha)] = m(\ln t + \ln k) \tag{3}$$

Analysis of Tables 1–3 leads to the conclusion that none of the related models in Table 2 can perfectly describe the kinetics of the $Fe(BPHA)_3$ decomposition.

Another attempt was to verify the equation proposed by Ng [13]

$$\mathrm{d}\alpha/\mathrm{d}t = k\alpha^{1-p}(1-\alpha)^{1-q} \tag{4}$$

According to Ng, any solid decomposition kinetic model may be described by eqn. (4), where k is the rate constant and p and q are temperature-independent parameters having values between zero and 1. However, our attempt to fit the experimental data to this equation was unfruitful.

Machado et al. [5] observed that three different kinetic models could describe the $Cr(BPHA)_3$ thermal decomposition equally well: the Avrami–Erofeev model, with $m = 4$ (model A); an autocatalytic model (model B); and the liquid phase formation model (model C). In the last two models, the important role played by one of the principal $Cr(BPHA)_3$ thermolysis products, the benzanilide, was emphasised. In fact, independent experiments carried out by mixing benzanilide with the complexes $Cr(BPHA)_3$ and $Fe(BPHA)_3$ prior to heating show a noticeable enhancement effect of the thermal decomposition for both the complexes and also show that this effect is dependent on benzanilide concentration. Furthermore, if two samples, composed of the chromium or iron chelate and pure benzanilide, respectively, are placed on a microscope slide close to each other, it can be observed that the melting of the benzanilide is followed by the immediate dissolution of the complex sample into the liquid phase (the melting point of benzanilide is 161.0 °C [14], and the thermal decomposition range for both complexes is 160–180 °C). Finally, microscopic observation of samples, using a platinum heater coupled to a microscope, showed the formation of small liquid regions which diffuse slowly until the whole system is in the liquid phase.

Model B presupposes an autocatalytic process, according to the following two-step scheme

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} + \mathrm{C} \tag{5}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} 2\mathrm{B} + \mathrm{C} \tag{6}$$

where A represents the reagent, B the benzanilide, and C the other decomposition products. The rate equation would be

$$\mathrm{dA}/\mathrm{d}t = -k_1\mathrm{A} - k_2\mathrm{AB} \tag{7}$$

or

$$\mathrm{d}\alpha/\mathrm{d}t = k_1(1-\alpha) + k_2 A_0 \alpha(1-\alpha) \tag{8}$$

where A_0 is the initial number of undecomposed molecules in moles. Integration of eqn. (8) yields

$$\alpha = [1 - \exp(-\delta t)]/[1 + (k_2 A_0/k_1)\exp(-\delta t)] \tag{9}$$

where $\delta = k_1 + k_2 A_0$. Using eqn. (8), it is easy to show that, since $2k_2 A_0 \gg k_1$

$$\alpha_{\max} = 0.50 - [k_1/(2k_2 A_0)] \approx 0.50 \tag{10}$$

This $\alpha_{\max}$ value is significantly lower than the experimental value observed for $\mathrm{Fe(BPHA)_3}$. Consequently, the attempt to fit the experimental curves to this model was unsuccessful.

Model C provided the best fit for the $\mathrm{Cr(BPHA)_3}$ experimental data. It presupposes, as a first step, that the reaction is a first-order process in the solid state. As the benzanilide is formed, it melts and partially dissolves the undecomposed complex, forming a liquid phase and the decomposition process is accelerated. This model can be represented by the following reaction schemes, both first-order

$$\mathrm{A_s} \xrightarrow{k_s} \mathrm{B} + \mathrm{C} \tag{11}$$

$$\mathrm{A_l} \xrightarrow{k_l} \mathrm{B} + \mathrm{C} \tag{12}$$

where $\mathrm{A_s}$ and $\mathrm{A_l}$ represent the original molecules in the solid and in the liquid states, respectively, and B and C are the products.

The variation of A with time may be expressed, as suggested by Bawn [15], by making use of the molecular solubility, S

$$S = \mathrm{A_l}/\mathrm{B} \tag{13}$$

It may then be shown that [5,16]

$$\alpha = (k_s/D)(\exp(Dt) - 1) \qquad \text{if } \alpha < \alpha_{\lim} \tag{14}$$

and

$$\alpha = (1 - \alpha_{\lim})\{1 - \exp[-k_l(t - t_{\lim})]\} + \alpha_{\lim} \qquad \text{if } \alpha > \alpha_{\lim} \tag{15}$$

where

$$D = k_l S - k_s(S + 1) \tag{16}$$

In the last expressions, $\alpha_{\lim}$ and $t_{\lim}$ correspond respectively to the values of decomposed fraction and the heating time when the chelate dissolution was completed, and are given by

$$\alpha_{\lim} = 1/(1 + S) \tag{17}$$

and

$$t_{\lim} = (1/D)\ \ln[(D/k_s)\alpha_{\lim} + 1] \tag{18}$$

It must be noted that for $\alpha = \alpha_{\lim}$, only the first-order reaction in the liquid phase (reaction (12)) takes place and it persists until all the reagent is consumed.

Equations (14)–(18) fit quite well with the experimental data for the Fe(BPHA)$_3$ thermal decomposition, as shown in Fig. 2, where the calculated curves are drawn as solid lines and the points are the experimental data. The value of $S = 0.35$ fitted a large number of the curves and, therefore, was taken for all the curves. The obtained rate constants are summarised in Table 4.

A measure of how adequate model C is to our experimental data can be obtained by supposing that the experimental values of α must be a linear function of the calculated α according to

$$\alpha_{\exp} = a\alpha_{\text{calc}} + b \tag{19}$$

with $a = 1$ and $b = 0$. Table 5 summarises the a and b values, as well as the linear correlation coefficients for eqn. (19) for the different temperatures studied. The results obtained confirm that model C agrees with the experimental data for the Fe(BPHA)$_3$ thermolysis.

The k_l and k_s values in Table 4 (with the exception of k_s at 170.0 °C) may be described by the Arrhenius equation, as shown in Fig. 3. The following expressions are obtained

$$k_s\ (\text{s}^{-1}) = (8.1 \times 10^{13})\ \exp(-156\ \text{kJ mol}^{-1}/RT) \tag{20}$$

$$k_l\ (\text{s}^{-1}) = (8.6 \times 10^{18})\ \exp(-178\ \text{kJ mol}^{-1}/RT) \tag{21}$$

The linear correlation coefficients for these equations are respectively 0.997 and 0.986.

The experimental value of the pre-exponential factor for reaction (12) ($A_l \approx 10^{19}$ s^{-1}) seems high for a process in the liquid phase. As suggested by

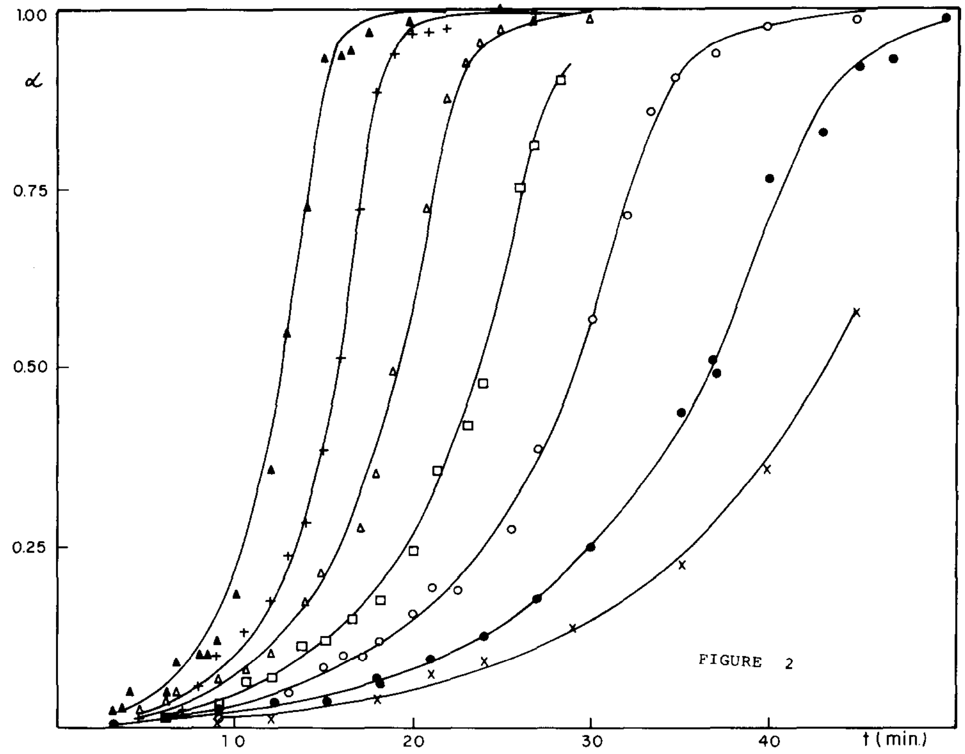

Fig. 2. Isothermal variations of the decomposed fraction α as a function of time t for temperatures of: ×, 160.0 °C; ●, 162.6 °C; ○, 164.2 °C; □, 166.2 °C; △, 168.0 °C; +, 170.0 °C; and ▲, 172.0 °C, according to model C.

TABLE 4

Kinetics parameters according to model C for $S = 0.35$

Temperature (°C)	$k_s \times 10^5$ (s^{-1})	$k_1 \times 10^3$ (s^{-1})
160.0	1.67	4.25
162.6	2.16	4.83
164.2	2.68	6.17
166.2	3.17	7.68
168.0	3.67	9.65
170.0	3.42	12.83
172.0	5.33	14.67

TABLE 5

Parameters for $\alpha_{max} = a\alpha_{calc} + b$ (eqn. (19))

T (°C)	160.0	162.6	164.2	166.2	168.0	170.0	172.0
a	0.988	0.997	0.994	0.996	1.006	1.000	0.998
b	0.005	0.002	0.002	−0.002	−0.001	−0.006	−0.003
r	0.996	0.996	0.999	0.995	0.998	0.998	0.997

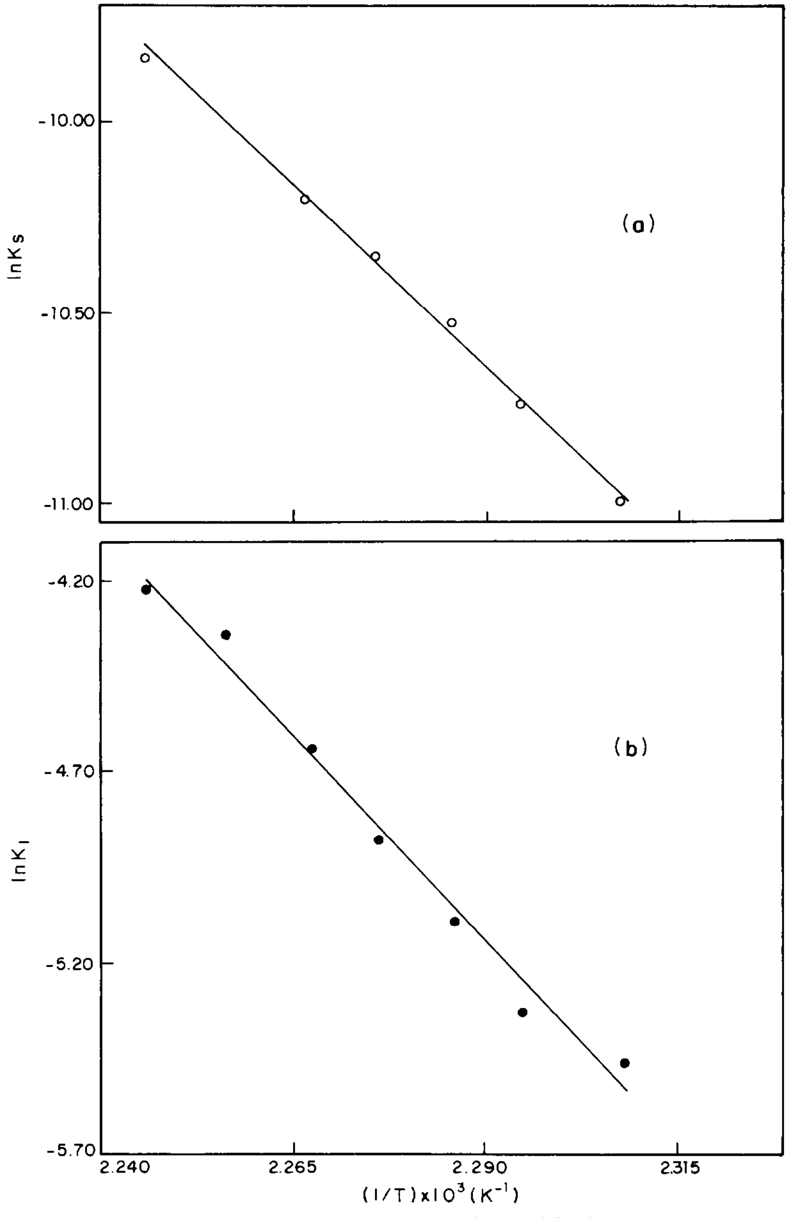

Fig. 3. Arrhenius plots for rate constants: a, k_s; and b, k_l.

Machado et al. [5] the liquid phase formation is probably not the only factor influencing the rate constant; the physical situation may rather be described as one in which the molecules of benzanilide influence the immediately surrounding undamaged complex molecules in such a way that one of them can decompose at a higher rate than in a normal lattice-site of the original solid.

TABLE 6

Experimental and theoretical α_{max} values

$Cr(BPHA)_3$				$Fe(BPHA)_3$			
Model A	Model B	Model C	Experimental	Model A	Model B	Model C	Experimental
0.49	0.50	0.50	0.49 ± 0.04	0.63	0.50	0.74	0.73 ± 0.04

A comparison between the experimental values of α_{max} for the $Fe(BPHA)_3$ and $Cr(BPHA)_3$ complexes, and those anticipated by the models A, B and C, explains why the three models describe the $Cr(BPHA)_3$ thermolysis equally well, whereas only model C is appropriate for the $Fe(BPHA)_3$ thermal decomposition. In the case of model A, it can be demonstrated that $\alpha_{max} = 1 - \exp[(1-m)/m]$; in other words, α_{max} changes in the range 0.39–0.63. For model B, α_{max} is approximately 0.50. Finally, for model C, according to eqns. (14), (15) and (17), $\alpha_{max} = 1/(1+S)$. These conclusions are shown in Table 6, where the tabulated value of α_{max} for $Cr(BPHA)_3$ is with $m = 4$, and in the case of $Fe(BPHA)_3$, with $m = \infty$.

Assuming that model C accurately describes the thermal decomposition for the two chelates, the high value for the molecular solubility ($S = 1.0$) in the case of $Cr(BPHA)_3$ would be viewed as the factor responsible for the casual adjustment to the models A and B. In the case of $Fe(BPHA)_3$, as $S = 0.35$, lower than the value found for $Cr(BPHA)_3$, the two models (A and B) do not fit the experimental curves, because near α_{max} these curves have more pronounced slopes than any simulated curve obtained with the models B or C.

CONCLUSIONS

The kinetics of the thermal decomposition of $Fe(BPHA)_3$ is not described by the models usually used in the study of solid thermolysis. Among the models used to describe the thermal decomposition of $Cr(BPHA)_3$, only the model which presupposes a liquid phase formation due to the melting of the principal decomposition product, the benzanilide, can be equally applied to the iron chelate.

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