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Thermal decomposition kinetics of solid iron(III) tris-*N*-*p*-nitrobenzoyl-*N*-phenylhydroxylamine

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Abstract

The thermal decomposition kinetics of iron(III) tris-*N*-*p*-nitrobenzoyl-*N*-phenylhydroxylamine was studied by the isothermal heating technique in the range 164–177°C. The principal non-gaseous stable products of the thermal decomposition were isolated and identified. The thermal decomposition process seems not to obey a single kinetic model in the full range of studied temperatures. Kinetic models that should account for the experimental evidence are discussed.

INTRODUCTION

The thermal decomposition kinetics of solid chromium(III) and iron(III) *N*-benzoyl-*N*-phenylhydroxylamine complexes, $Cr(BPHA)_3$ and $Fe(BPHA)_3$, respectively, were studied by Machado et al. [1, 2]. For these compounds, it was observed that the kinetic equations usually used in the study of solid thermal decompositions [3] are not adequate to describe the experimental results. For both complexes, it was shown that only one of the models proposed by Machado and collaborators, involving the formation of a liquid phase, was able to describe the experimental data. According to this autocatalytic process, the thermal decomposition of $Cr(BPHA)_3$ and $Fe(BPHA)_3$ could be interpreted in terms of the formation of a liquid phase, created as a consequence of the melting of one of the principal non–gaseous stable products, the benzanilide, as the chelate molecules are being decomposed in the initial solid phase; this dissolves the complexes, thus resulting in a faster rate of a decomposition reaction.

In the present work, we have studied the thermal decomposition of $Fe(p\text{-}NO_2\text{–}BPHA)_3$ in order to gain a better knowledge of the decomposition kinetics of this class of compounds. Because the structural modification was introduced in the site far removed from the coordination sphere, it is

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not expected that the temperature range for the thermal decomposition should be significantly different from that for the Cr(BPHA)$_3$ and Fe(BPHA)$_3$ complexes. However, because the *p*-NO$_2$–benzanilide has a melting point significantly higher (210°C) than the melting point of the benzanilide (160°C), we would expect that the decomposition process should be affected.

EXPERIMENTAL

The *N*-*p*-nitrobenzoyl-*N*-phenylhydroxylamine (*p*-NO$_2$–BPHA) ligand was synthesized as described by Alimarin et al. [4] and Lukaschewitsch [5], with some modifications. The product, in the form of flocculous crystals, presented a melting point in the range 161–163°C. The elemental analysis led to the following results: calculated content per molecule of $C_{13}H_{10}N_2O_4$ in wt%: $C = 60.50$, $H = 3.88$ and $N = 10.85$; found: $C = 59.66$, $H = 3.91$ and $N = 10.75$. The reaction yield was 85%. The iron complex Fe(*p*-NO$_2$–BPHA)$_3$ was synthesized according to the method described by Chan and Moshier [6] for Fe(BPHA)$_3$, with appropriate modifications, and purified by chromatography using cellulose as stationary phase and toluene as eluent. After solvent evaporation, the complex was vacuum-dried overnight and ground to pass 250 mesh. The elemental analysis led to the following results: calculated content per molecule of $C_{39}H_{27}N_6O_{12}Fe$ in wt%: $C = 56.59$, $H = 3.26$ and $N = 10.66$; found: $C = 56.70$, $H = 3.38$ and $N = 10.20$.

The principal stable non-gaseous products of the Fe(*p*-NO$_2$–BPHA)$_3$ thermal decomposition were isolated using a chromatographic technique, with silica as the stationary phase and a mixture of solvents of different polarities (toluene, chloroform, ethylacetate, methanol and acetic acid) as eluents.

The eluted fractions were separated and identified by thin layer chromatography, infrared spectroscopy (Perkin-Elmer, mod. 467), melting point (Mettler, models FP5 and FP52), NMR (Varian, model EM360) and powder X-ray diffractometry (Rigaku). The following non-gaseous stable products were separated and identified: *p*-NO$_2$–benzoic acid, iron(III) *p*-NO$_2$–benzoate and *p*-NO$_2$–benzanilide, the last being the principal thermal decomposition product.

The thermal decomposition experiments and the determination of the undecomposed fraction $(1 - \alpha)$ were carried out as described elsewhere [1, 2]. For the absorption measurements, the absorption band centred at $\lambda_{max} = 450$ nm, with $\varepsilon = 6850\ l^{-1}\ mol^{-1}\ cm^{-1}$ was used.

RESULTS AND DISCUSSION

The TG curve for the Fe(*p*-NO$_2$–BPHA)$_3$ complex, obtained at a 10°C min^{-1} heating rate in air atmosphere, is shown in Fig. 1. We can see

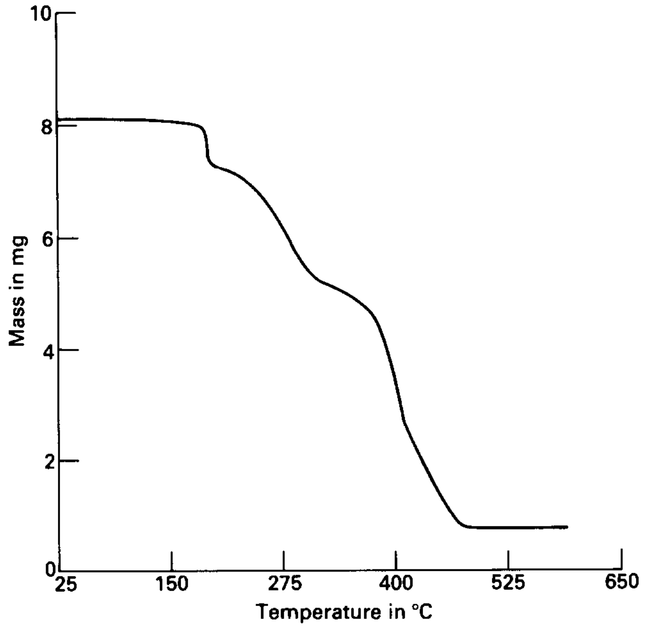

Fig. 1. TG curve of Fe(p-NO_2–BPHA)$_3$.

that the initial decomposition occurs at 160.0°C, with a mass loss of 8.2%. Therefore, a series of isothermal heating experiments was performed in the range 164.0–177.0°C and reported in terms of the decomposed fraction α.

A qualitative analysis of the isothermals suggests that the kinetics of the thermal decomposition of Fe(p-NO_2–BPHA)$_3$ is complex and unlikely to obey a single kinetic equation. We can pinpoint three temperature intervals.

(i) For the lower temperatures (164.0 and 165.0°C), the α against t curves show an induction period up to $\alpha \approx 0.15$. During this period α rapidly increases with t until the saturation value is attained and then the curve presents a typical deceleratory behaviour, i.e. $d\alpha/dt$ decreases as the heating time increases.

(ii) For the temperatures 166.0 and 170.0°C, the induction period is not present and the α against t curves are deceleratory.

(iii) Finally, the 175.0 and 177.0°C experiments display the well-known sigmoidal shape, characteristic of an autocatalytic process.

From the preceeding discussion, it is apparent that the kinetics of the thermal decomposition of Fe(p-NO_2–BPHA)$_3$ is quite different from that observed for Cr(BPHA)$_3$ [1] and Fe(BPHA)$_3$ [2], for which the α against t curves are typical of an autocatalytic process over the full range of studied temperatures.

Table 1 summarizes the principal kinetic models used in the study of solid thermal decomposition [2, 3, 7].

TABLE 1

Kinetic equations used in thermal decomposition reactions in the solid state

Controlling process	Symbols	Equations	Shape of $\alpha - t$ curves
Diffusion	D_1	$\alpha^2 = kt$	Deceleratory
	D_2	$(1-\alpha)\ln(1-\alpha) + \alpha = kt$	Deceleratory
	D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Deceleratory
	D_4	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	Deceleratory
Phase-boundary reaction	R_1	$1-(1-\alpha) = kt$	Deceleratory
	R_2	$1-(1-\alpha)^{1/2} = kt$	Deceleratory
	R_3	$1-(1-\alpha)^{1/3} = kt$	Deceleratory
Nucleation and nuclei growth	A_m	$-[\ln(1-\alpha)]^{1/m} = kt$ $m = 2, 3, 4, \ldots$	Sigmoidal
	A_n	$\ln[\alpha/(1-\alpha)] = kt + C, k > 1$	Sigmoidal
	A_x	$\ln[\alpha/(1-\alpha)] = k \ln t + C$ $k > 1$	Sigmoidal
	P_n	$\alpha^{1/n} = kt$	Acceleratory
	F_1	$-\ln(1-\alpha) = kt$	Deceleratory

The mechanisms controlled by diffusion, phase-boundary reaction and the model F_1 are compatible with our experimental results obtained for the temperature interval 164.0–170.0°C. The corresponding kinetic equations were treated by a linear regression program, according to the general expression

$$F(\alpha) = kt + k_0 \tag{1}$$

where k_0 accounts for the observed induction period. Equation (1) does not describe α values lower than 0.15. The linear correlation coefficients displayed in Table 2 suggest that the R_3 and F_1 models are the most appropriate to describe the experimental results.

It can be seen that the best r values for the four temperatures are for the R_3 and F_1 models. Both models reproduce quite well our experimental data,

TABLE 2

Linear correlation coefficients r to fit equation $f(\alpha) = kt + k_0$ ($\alpha > 0.15$)

Temp./°C	Model							
	D_1	D_2	D_3	D_4	R_1	R_2	R_3	F_1
164.0	0.9956	0.9963	0.9767	0.9920	0.9628	0.9927	0.9967	0.9943
165.0	0.9940	0.9962	0.9733	0.9932	0.9641	0.9938	0.9978	0.9967
166.0	0.9969	0.9810	0.9700	0.9901	0.9728	0.9940	0.9965	0.9986
170.0	0.9780	0.9930	0.9926	0.9939	0.9429	0.9826	0.9923	0.9993

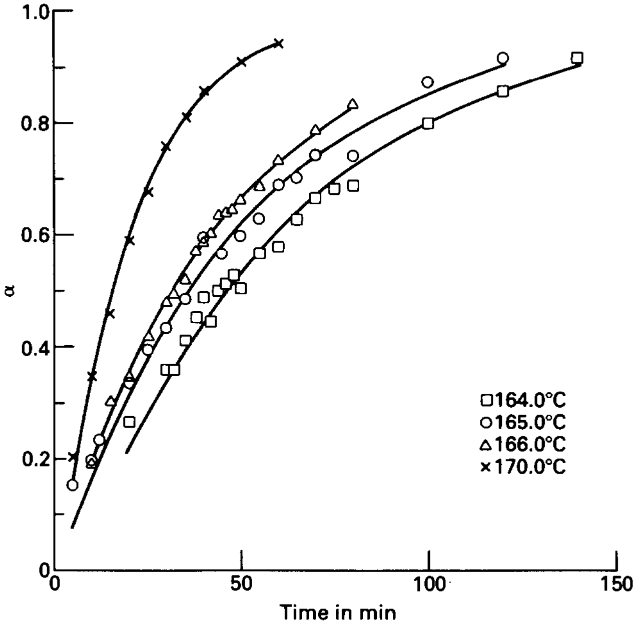

Fig. 2. R_3 plot for the isothermal decomposition of Fe(p-NO_2–BPHA)$_3$.

as shown in Figs. 2 and 3, where the calculated curves are drawn as solid lines and the points are the experimental results. The calculated rate constants and standard deviations s are summarized in Table 3.

The k values may be described by the Arrhenius law, as shown in Fig. 4 according to the expressions

$$k_{F_1}/s^{-1} = 5.0 \times 10^{30} \exp(-286.6\ \text{kJ mol}^{-1}/RT) \qquad (2)$$

and

$$k_{R_3}/s^{-1} = 8.2 \times 10^{26} \exp(-260.2\ \text{kJ mol}^{-1}/RT) \qquad (3)$$

It should be mentioned that other workers have obtained high values for the pre-exponential factor in the study of thermal decomposition reactions in the solid state [7–10].

For the experiments at the two higher temperatures (175.0 and 177.0°C), the mechanism of the thermolysis seems to be very different from the experiments at lower temperatures. The α against t curves at 175.0 and 177.0°C present the well-known sigmoidal shape of an autocatalytic process. The decomposition is very rapid, attaining about 70% after a heating time of only 10 min, and then the reaction rates decrease markedly. The maximum $d\alpha/dt$ occurs for $\alpha \approx 0.50$. As can be seen in Table 2, only the A_m, A_n and A_x models are compatible with α against t curves with these characteristics. However, an attempt to fit the curves to these models was unsuccessful.

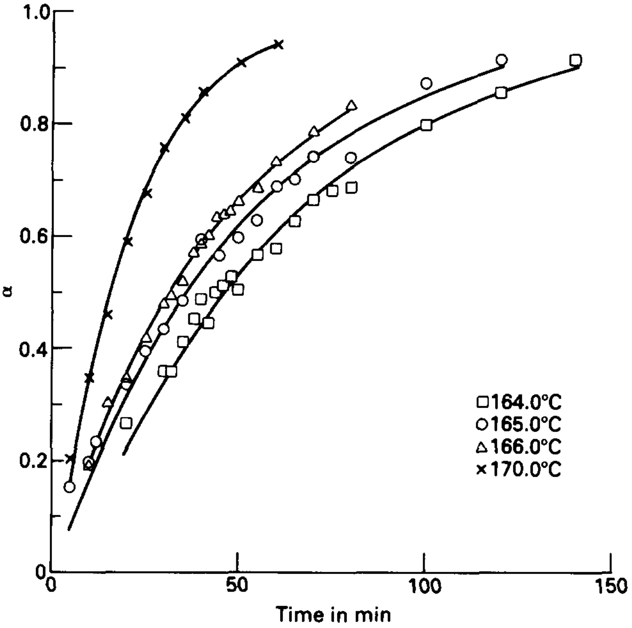

Fig. 3. F_1 plot for the isothermal decomposition of $Fe(p\text{-}NO_2\text{-}BPHA)_3$.

Machado et al. [1, 2] used two other kinetic models to interpret the $Cr(BPHA)_3$ and $Fe(BPHA)_3$ thermolysis. These two models of a first-order process have autocatalytic characteristics and the α against t curves present a sigmoidal shape, as observed here for 175.0 and 177.0°C.

The first model, named the "autocatalytic model" (Model A) presupposes a typical autocatalytic process, leading to the kinetic equation

$$\alpha = [1 - \exp(-\delta t)]/[1 + (k_2 A_0/k_1)\exp(-\delta t)] \tag{4}$$

where $\delta = k_1 + k_2 A_0$, k_1 and k_2 are the rate constants, and A_0 is the initial concentration of undecomposed molecules.

The second model, named the "liquid phase formation model" (Model B) presupposes the formation of a liquid phase during the decomposition process.

TABLE 3

Constant rates, according to F_1 and R_3 models

Model	Parameter	Temperature in °C			
		164.0	165.0	166.0	170.0
F_1	$k \times 10^3/s^{-1}$	2.87	3.33	3.67	8.17
	s	0.021	0.019	0.012	0.016
R_3	$k \times 10^5/s^{-1}$	6.43	7.50	9.13	17.00
	s	0.021	0.013	0.016	0.029

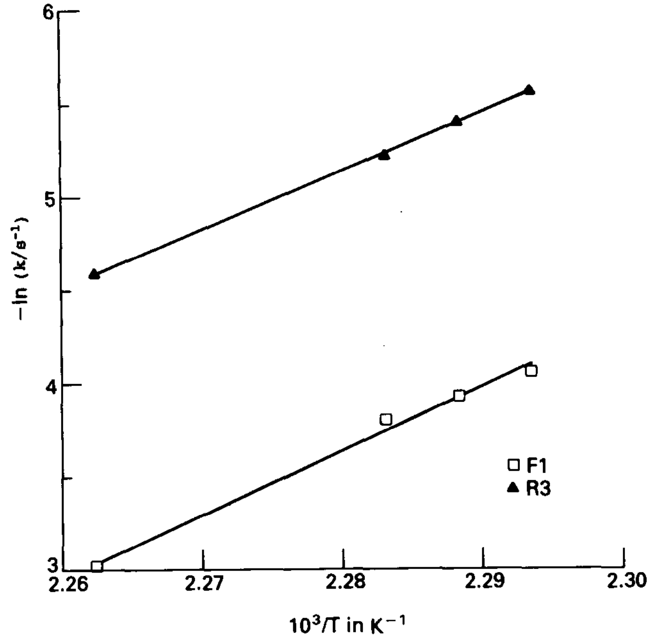

Fig. 4. Arrhenius plots for the isothermal decomposition of Fe(p-NO_2BPHA)$_3$.

It can be demonstrated [1] that

$$\alpha = (k_s/D)[\exp(Dt) - 1] \qquad \text{for } \alpha < \alpha_{\text{lim}} \qquad (5)$$

and

$$\alpha = (1 - \alpha_{\text{lim}})\{1 - \exp[-k_l(t - t_{\text{lim}})]\} + \alpha_{\text{lim}} \qquad \text{for } \alpha > \alpha_{\text{lim}} \qquad (6)$$

where k_s and k_l are the rate constants related to the solid and liquid phases, respectively, S is the solubility, $D = k_l S - k_s(S + 1)$, $\alpha_{\text{lim}} = 1/(1 + S)$ and $t_{\text{lim}} = (1/D)\ \ln[(D/k_s)\alpha_{\text{lim}} + 1]$; k_s, k_l and S are adjustable parameters.

Figure 5 suggests that both models fit quite well the experimental data for $T = 175.0$°C. However, there are some arguments which recommend the rejection of these models. In the case of Model A, the k_1 and k_2A_0 calculated values were 0.078 min^{-1} and 0.125 min^{-1}, respectively. These results mean that the maximum reaction rate would be at $\alpha = \alpha_{\text{max}} = 0.5 - k_1/(2k_2A_0) \approx 0.19$; but the experimental result is $\alpha_{\text{max}} \approx 0.50$. In the case of Model B no product was identified which was liquid in the temperature range of decomposition. Furthermore, the calculated k_s and k_l values are of the same order of magnitude (0.085 and 0.170 min^{-1}), while the expected relation between these two constants is $k_l \gg k_s$. Owing to the strong acceleratory effect observed for $T = 177.0$°C, it was impossible to fit the α against t curve to eqn. (4) (Model A) or eqns. (5) and (6) (Model B).

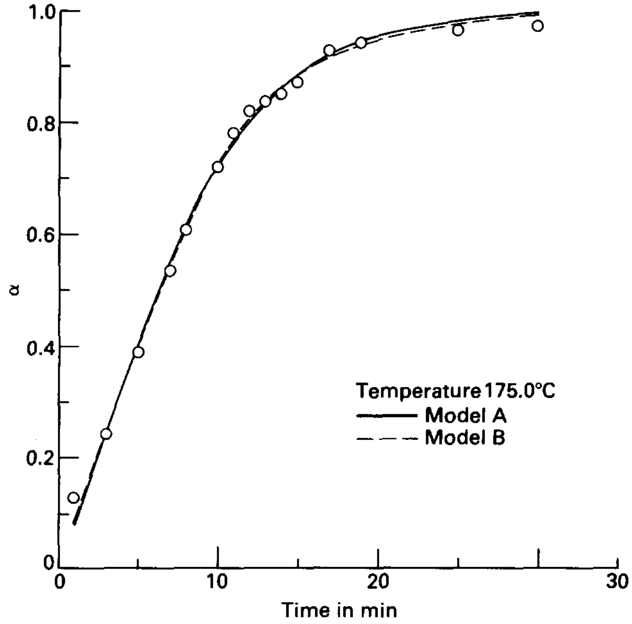

Fig. 5. Isothermal decomposition of Fe(p-NO$_2$–BPHA)$_3$ analysed according to the "autocatalytic" (A) and "liquid phase formation" (B) models.

CONCLUSIONS

The thermal decomposition kinetics of the Fe(p-NO$_2$–BPHA)$_3$ complex does not follow a single kinetic model in the full range of studied temperatures. An induction period ($0 < \alpha < 0.15$) observed at lower temperatures (164.0 and 165.0°C) was not observed at higher temperatures.

The α against t curves at 164.0, 165.0, 166.0 and 170.0°C are adequately fitted to the equation $1-(1-\alpha)^{1/3} = kt$ (phase-boundary reaction) and $-\ln(1-\alpha) = kt$ (nucleation and nuclei growth), for $0.15 \leq \alpha \leq 0.98$ values.

For the higher temperatures (175.0 and 177.0°C), the α against t curves show a sigmoidal shape typical of an autocatalytic process, but an attempt to fit these curves to the appropriate equations related to these processes was unsuccessful.

Although the curve for 175.0°C was in fairly close accord with the alternative models suggested by Machado et al. [1, 2] for the Cr(BPHA)$_3$ and Fe(BPHA)$_3$ complexes, there are strong arguments which lead to the rejection those models.

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