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Thermal behaviour and isothermal kinetics of rhodium(II) acetate

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Abstract

The thermal decomposition of solid rhodium(II) acetate was studied by isothermal TG. Kinetic analysis of the isothermal data showed that the complex decomposition in the range 198.0–210.5°C occurs according to a Prout–Tompkins (A_n) law. The isothermal curves are better fitted using a non-linear least square method. The activation energy found was 162.7 kJ mol^{-1}. At temperatures higher than 210.5°C the decomposition is strongly accelerated and no kinetic study was available.

Keywords: Isothermal; Kinetics; Mechanism; Rhodium(II) carboxylates; Solid State; Thermal decomposition

1. Introduction

The discovery of antitumor activity of rhodium(II) carboxylates in 1972 [1,2] opened up a variety of interesting areas of research with these kind of compounds. Several studies of thermal decomposition have been reported in the literature [3–9], but kinetic decomposition studies of rhodium(II) tetracarboxylates have not been reported. The thermal behaviour of rhodium(II) acetate, $Rh_2(Ac)_4$, can be described as follows: the first stage of decomposition occurs at temperatures above 200.0°C, producing Rh(0); in the second stage, there is oxidation of Rh (0) to Rh_2O_3 [4,8].

In the present work, the thermal behaviour and kinetics of the decomposition of $Rh_2(Ac)_4$ has been studied. It was observed that the isothermal decomposition process is drastically influenced by the temperature. For temperatures between 198.0°C and 210.5°C, the formation of RhO_2 was observed according to a rate equation compatible with the branching chain nucleation model of Prout–Tompkins [10]. On the other hand, at temperatures higher than 210.5°C, the final product of decomposition is Rh_2O_3, and because of the higher rate of this process, it was not possible to carry out kinetic studies with this technique.

2. Experimental

$Rh_2(Ac)_4$ was synthesised as described by Rempel et al. [11]. The compound was ground to pass 100 mesh. Thermal decomposition experiments were measured on a TG-50 Mettler TA-4000 system, using dynamic air atmosphere; 7.0 mg samples packed in alumina crucible of 70 µl were used. The samples were weighed at 105.0°C, in order to eliminate humidity or solvents. The isothermal curves were reported at temperatures between 198.0°C and 251.0°C.

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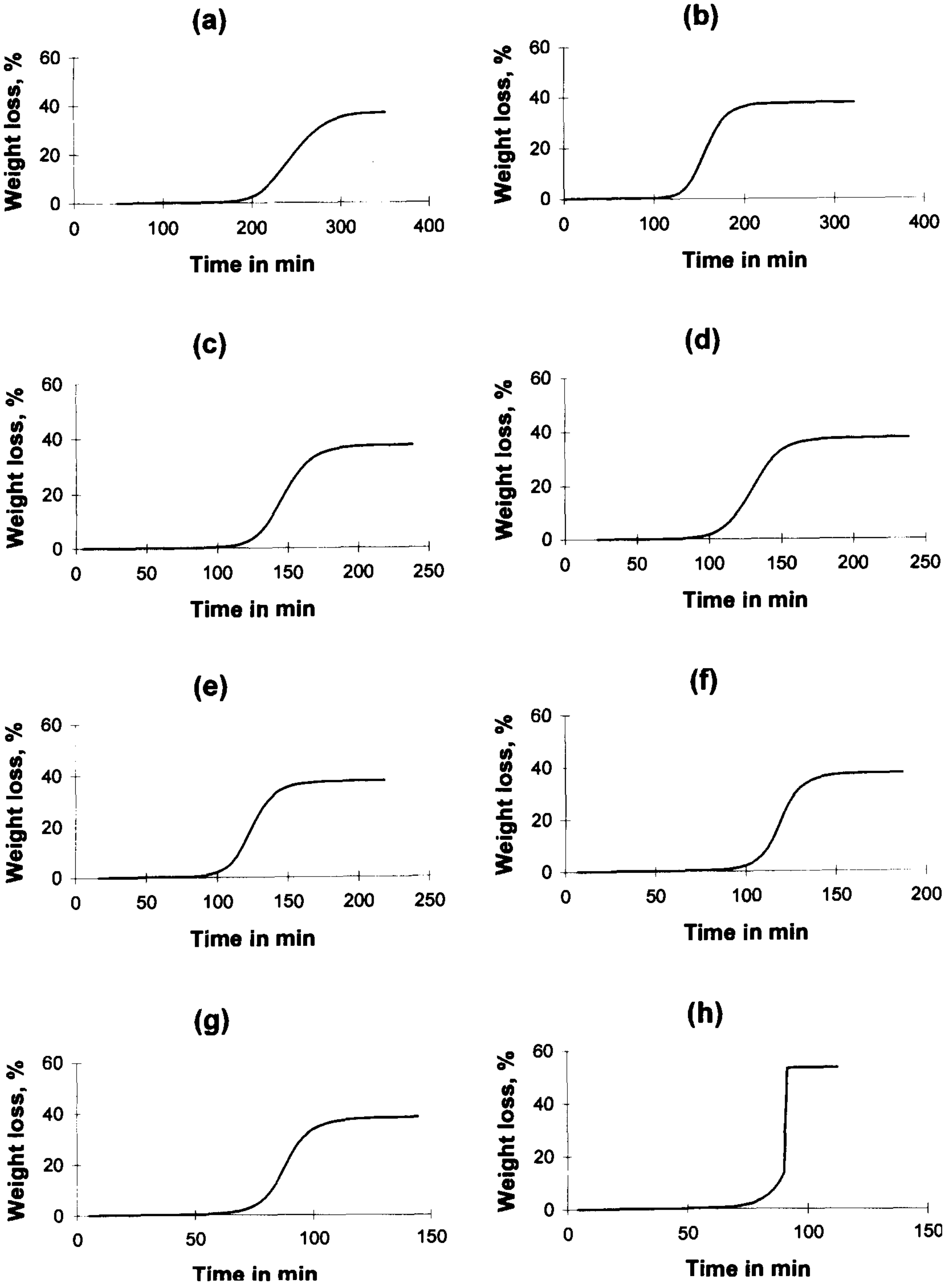

Fig. 1. Isothermal mass loss runs for rhodium(II) acetate, in air. (a) 198.0°C; (b) 202.5°C; (c) 203.5°C; (d) 205.0°C; (e) 207.0°C; (f) 209.0°C (g) 210.5°C; (h) 212.0°C.

The IR spectra were measured in a Perkin-Elmer model 283B spectrophotometer, using CsI dispersion mulls. Elemental analyses were on a Perkin-Elmer 2400 CHN. The wide Angle X-Ray Diffraction (XRD) patterns were obtained using a Rigaku instrument with Cukα radiation, 30 mA and 40 kV, and a scanning rate of 4° min^{-1}.

3. Results and discussion

The XRD pattern of the residue obtained after heating the sample at 300°C showed that Rh(0) was formed. The weight loss observed in the TG curve was also consistent with Rh(0). Between 300 and 600°C, a gain of mass was observed. The final product at 900°C was characterised by XRD and IR and the results suggested the formation of Rh_2O_3, as reported in literature [12], but the gain of mass (experimental =17%; expected =23%) indicated that oxidation was not complete.

Fig. 1 shows the TG curves measured under isothermal conditions for temperatures between 198.0°C and 212.0°C. The results show the following:

1. an induction period of 60–100 min;
2. the final product had approximately 62% of the starting mass, independently of the temperature. The residue displayed thermal stability when heating was maintained for 3 h.

The weight of this residue is compatible with the formation of RhO_2 (experimental: 62.2±0.2%, calculated: 61.1%). The residue was also characterised by XRD pattern, IR and CHN analysis. The CHN results showed that there was no hydrogen in the sample and that the percentage of carbon was always less than 1%. The IR spectrum presented only a large peak at 550 cm^{-1}, in accordance with the oxide formation. The XRD patterns was interpreted as amorphous material as suggested by the IR spectra at low frequencies.

The decomposition fractions, α, were determined by:

$$\alpha = \frac{m_i - m_t}{m_i - m_\infty} \tag{1}$$

where m_i = initial mass, m_t = mass in the time t and m_∞ = final mass.

Table 1
Values of α_{max} for the thermal decomposition of $Rh_2(Ac)_4$

T/°C	198.0	202.5	203.5	205.0	207.0	209.0	210.5
α_{max}	0.49	0.46	0.49	0.52	0.43	0.49	0.46

The isothermal curves of α versus t show a sigmoidal form, characteristic of an autocatalytic process. The values obtained for α_{max}, (α for maximum $d\alpha/dt$) are listed in Table 1. These results seems to suggest that α_{max} is temperature independent, implying that perhaps the same kinetic model describes the behaviour of all curves. The average value of α_{max}, 0.48± 0.03, suggests a kinetic model where the rate of decomposition is a maximum when α=0.50.

In accordance with a kinetic model earlier described [13,14], the present study can be interpreted as follows (model B):

$$A(s) \xrightarrow{k_1} B + C(g) + \ldots \tag{2}$$

$$A(s) + B \xrightarrow{k_2} 2B + C(g) + \ldots \tag{3}$$

where $k_2 >> k_1$.

This model leads to the equation:

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

where $\delta = k_1 + k_2 A_0$ and A_0= number of moles of undecomposed A when t=0. It can be shown that in this case:

$$\alpha_{max} = 0.5 - \frac{k_1}{2k_2 A_0} \approx 0.5 \tag{5}$$

In all the temperatures studied, Eq. (4) fits quite well the experimental data, as shown in Fig. 2, where the theoretical curves are represented by the solid line and the point corresponds to the experimental data. To fit those curves we use the following relation:

$$t = t_{exp} - t_0 \tag{6}$$

where t_{exp} is the real time of heating, and t_0 is the value of t_{exp} when $|dm/dt| > 2.10^{-5}$ mg s^{-1}. For all the temperatures studied, the α value at t_0, α_0, was found to be close to 0,005. As the value of α_0 is different from zero, the experimental data were compared to the α value defined by:

$$\alpha_{calc} = \alpha(1 - \alpha_0) + \alpha_0 \tag{7}$$

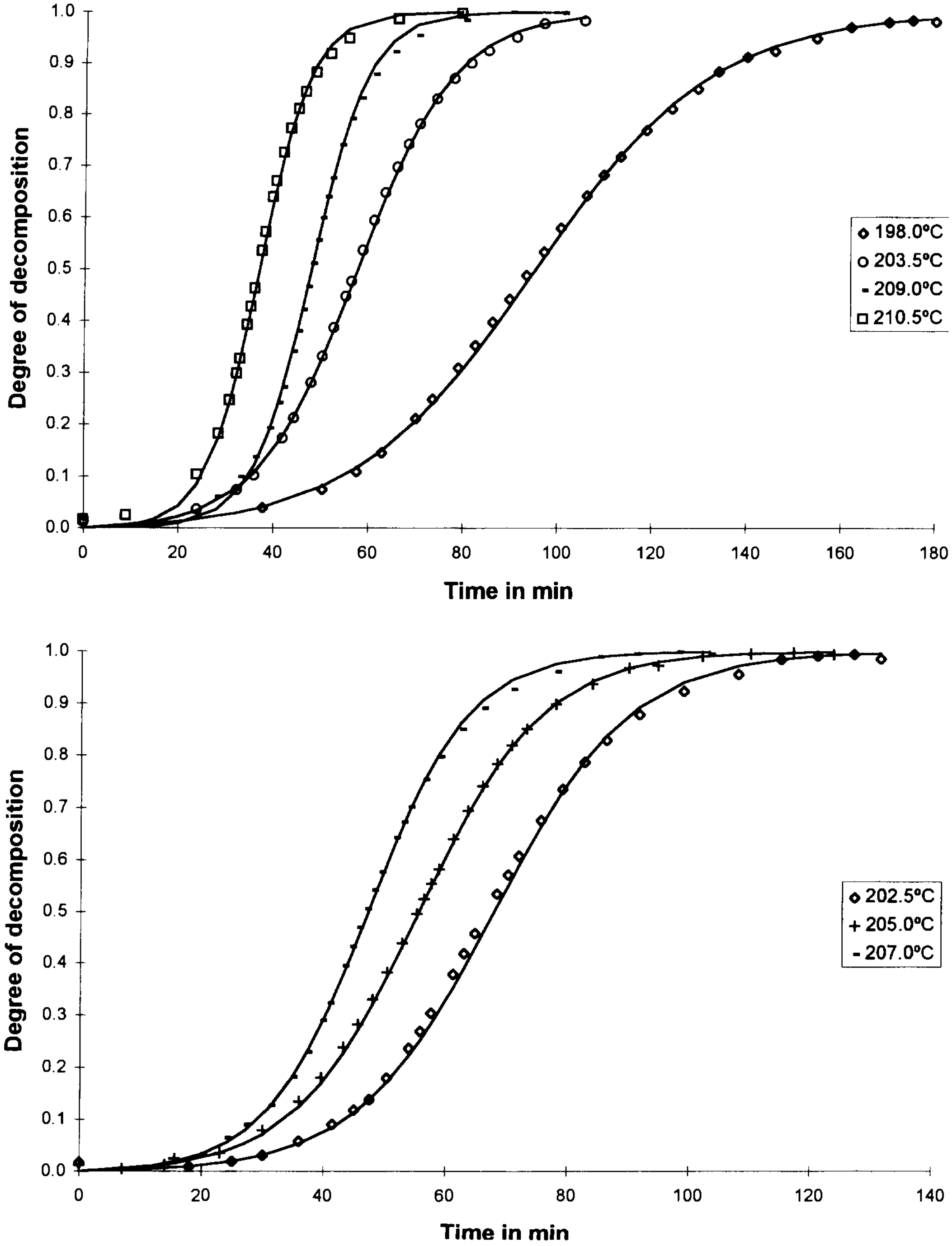

Fig. 2. Plots of the autocatalytic (B) model for the isothermal decomposition of rhodium(II) acetate.

Table 2
Parameters obtained after the fit of experimental α curves versus t, in accordance with model B.

Temperature/C	$k_1 \times 10^6/s^{-1}$	$k_2A_0 \times 10^3/s^{-1}$	Δ%
198.0	5.83	0.87	0.90
202.5	3.50	1.48	1.14
203.5	6.17	1.60	0.84
205.0	7.00	1.63	0.29
207.0	6.83	2.00	0.98
209.0	1.00	2.75	1.05
210.5	3.67	3.02	0.89

Table 3
Linear correlation coefficients, r, and % to fit Eq. (8).

Temp/°C	Model					
	A_3		A_n		A_x	
	r	Δ%	r	Δ%	r	Δ%
198.0	0.9959	2.1	0. 9982	1.3	0.9845	3.9
202.5	0.9856	3.7	0.9912	2.7	0.9971	2.4
203.5	0.9825	4.3	0.9953	2.0	0.9850	4.0
205.0	0.9803	4.9	0.9944	2.3	0.9614	6.2
207.0	0.9822	4.2	0.9945	2.5	0.9937	2.7
209.0	0.9747	5.9	0.9939	3.5	0.9901	3.7
210.5	0.9837	4.9	0.9950	3.0	0.9289	9.1

The values of k_1,k_2, A_0 and Δ% obtained from the fits are listed in Table 2, where Δ% is:

$$\Delta\% = \sqrt{\frac{\chi^2}{N}} \times 100 \qquad (8)$$

where N is the number of experimental points.

Table 2 shows that although the Δ% values indicate average standard deviations around 1%, the values of k_1 change in a random way with the temperature. Hence, it seems that the model described by Eq. (4) is not appropriate to the present result, and so another model has to be investigated.

Three of the models frequently used in solid decomposition studies present $\alpha_{\max}$ =0.50 [15]. They are the Prout–Tompkins model (A_n), the Prout–Tompkins modified model (A_x) and the Avrami–Erofeev model with m =3(A_3). The first two models correspond to nucleation process in branching chains with nuclear growth in one or two dimensions and with overlapping of growth nuclei. The third model describes the random nucleation according to a potency law, followed by nuclear growing in three dimensions with the overlapping of growth nuclei.

A general equation for the three models can be written as:

$$F(\alpha) = kt + k_0 \qquad (9)$$

where t is given by Eq. (6). Using Eq. (7), the $F(\alpha)$ values, for these three models were treated by a linear regression program. The linear correlation coefficients (r) and the corresponding values obtained for Δ% are shown in Table 3. Although the model A_n shows r values higher than 0.9900 for all temperatures and, with the exception of 202.5°C, the r values obtained with this model are better than those calculated for the other two models, it doesn't reproduce quite well the experimental curves. The Δ% values for this model are quite higher than the Δ% values obtained by model B. Consequently, the α versus t curves calculated do not reproduce quite well the experimental data. Besides, the k values cannot be described by the Arrhenius law (the linear correlation coefficient between ln k and T^{-1} is 0.86).

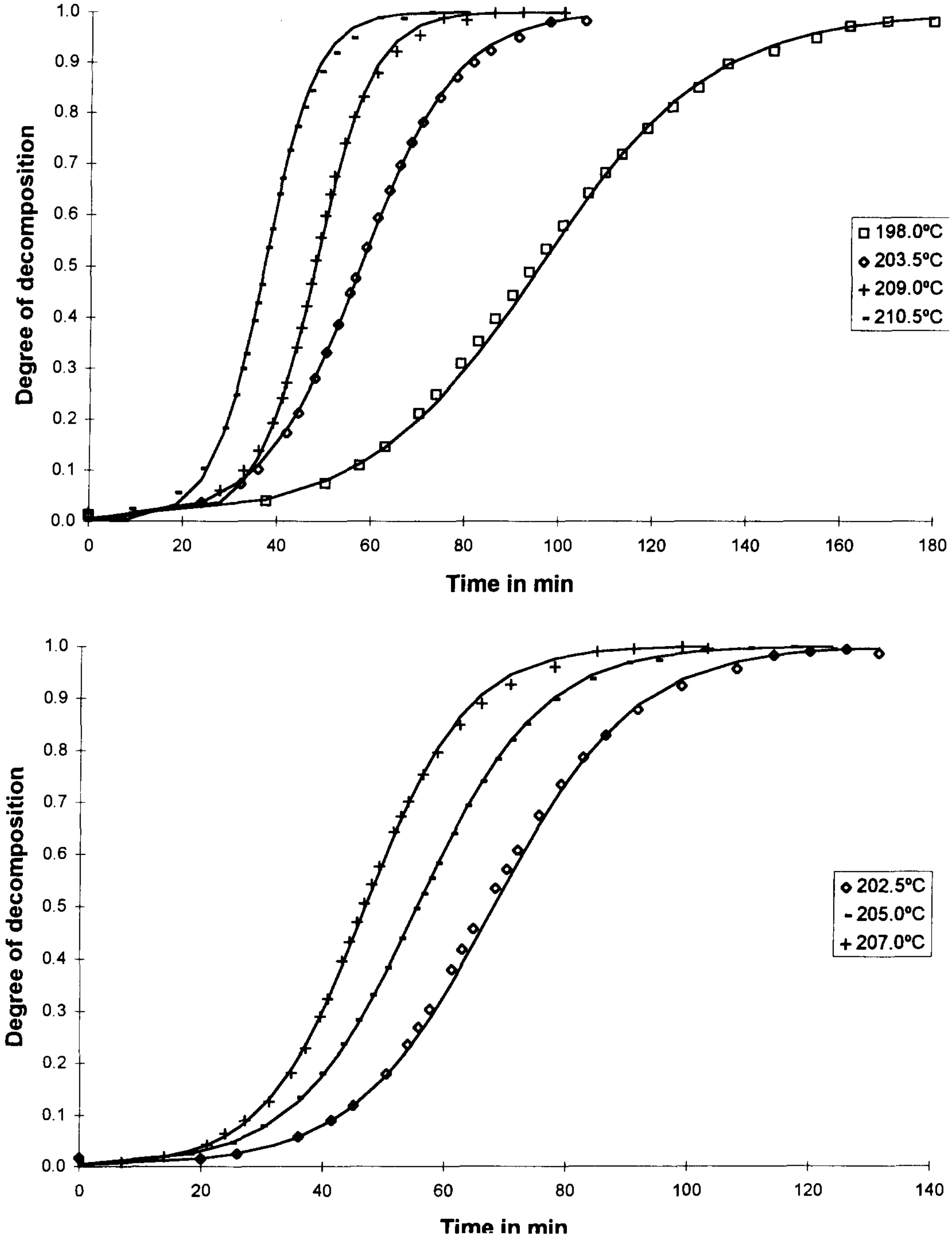

Fig. 3. Plots of the Prout–Tompkins (A_n) equation for the isothermal decomposition of rhodium(II) acetate.

Table 4
Values of k, k_0 and $\Delta\%$ obtained in the fit of Eq. (10) of the experimental data

Temperature/°C	$k\times10^3/\mathrm{s}^{-1}$	$-k_0$	$\Delta\%$
198.0	0.90	5.18	1.09
202.5	1.45	5.93	1.08
203.5	1.62	5.60	0.93
205.0	1.65	5.50	0.35
207.0	2.00	5.64	1.10
209.0	2.72	7.83	1.05
210.5	3.08	6.85	0.99

We attempted to obtain theoretical curves closer to the experimental results with a non-linear fit. In fact, in this case the linear regression method is an indirect fit, because instead of comparing the values of α_{exp} and $\alpha_{\mathrm{calculated}}$, it compares the corresponding $F(\alpha)$ values.The α values in A_n equation are given by:

$$\alpha = (1 + \exp - (kt + k_0))^{-1} \tag{10}$$

Using Eq. (10), Eq. (7) and Eq. (6) and a non-linear least square method we fit the experimental data. The curves obtained are shown in Fig. 3, where the points represent the experimental results and the solid line describe the theoretical curves. The k, k_0 and $\Delta\%$ values determined are listed in Table 4.

The $\Delta\%$ values are comparable with those calculated by model B (average deviation of 1% between experimental and calculated results). The rate constants obtained are described by Arrhenius law, in accordance with the following expression:

$$k/s^{-1} = 3.7 \times 10^{14}\exp\left(\frac{-162.7\,\mathrm{kJ\,mol^{-1}}}{RT}\right) \tag{11}$$

and the linear correlation coefficient for the ln k versus T^{-1} curve was 0.994.

At temperatures higher than 210.5°C, the thermal behaviour of $Rh_2(Ac)_4$ drastically changes, as can be seen by comparing Fig. 1 (g) and (h). Above 210.5°C, a fast acceleratory process was observed at the beginning of the decomposition, with a loss of mass higher than the one observed at lower temperatures. The α_{max} values (between 0.60 and 0.75) are different from those obtained at lower temperatures. As the thermal decomposition is extremely fast above 210.5°C, it was not possible to perform kinetic studies at such temperatures. For example, α varies from around 0.20 to about 0.80 in <1 min.

4. Conclusions

The thermal behaviour of $Rh_2(Ac)_4$, in air, is markedly modified by the temperature. For temperatures till 210.5°C the residue obtained is RhO_2, and the process can be explained by the Prout–Tompkins law, with an activation energy of 162.7 kJ mol^{-1} and pre-exponential factor of 3.7×10^{14} s^{-1}. The usual procedure to fit the isothermal curves α versus t by linear regression was not adequate. The fit of these curves was improved using a non-linear least square method.

At temperatures higher than 210.5°C, an increase in mass loss during the thermal decomposition was observed, and the final product is Rh(s). The process is strongly accelerated at these temperatures and for this reason it was not possible to measure the kinetics by thermogravimetric techniques.

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