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Note

NON-ISOTHERMAL DECOMPOSITION KINETICS OF A MONONUCLEAR COORDINATION COMPOUND OF Fe(II)

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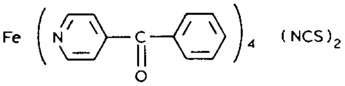
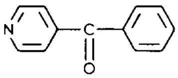
A non-isothermal kinetic study is presented concerning the thermal decomposition of the compound.



A previous paper [1] reported the results of a non-isothermal kinetic study concerning the heterogeneous thermal decomposition of some coordination compounds with the general formula $Me^{II}L_pX_2$ with $p = 2$ or 4, X is NCS or Cl and L is



Following our research, this note deals with the non-isothermal decomposition kinetics of $FeL_4(NCS)_2$.

EXPERIMENTAL

$FeL_4(NCS)_2$ powders synthesized according to a method described elsewhere [2] were used. The average crystallite sizes were evaluated from the X-ray powder diffractogram using Scherrer's formula [3]. The diffractogram was recorded using a Philips (PW 1450) X-ray diffractometer, and chromium $K\alpha$ radiation.

The heating curves in a static air atmosphere were recorded using a Paulik–Paulik–Erdey derivatograph with various heating rates between 2.77 and 9.84 K min^{-1}.

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To evaluate the non-isothermal kinetic parameters, a recently worked out iterative method was used [4].

RESULTS AND DISCUSSIONS

The most intense line in the X-ray powder diffractogram is located at 4.17 Å. For this line, using Scherrer's formulae, we obtained a value of 27 Å for the mean crystallite size.

According to the TG curves the thermal decomposition of $FeL_4(NCS)_2$ occurs in two steps as shown by the following equations. (The figures above the arrows indicate the temperatures (in degrees kelvin) corresponding to the maximum reaction rates.)

(i) $\beta_1 = 2.77$ K min^{-1}

$$FeL_4(NCS)_2(s) \xrightarrow{496.3} FeL_{1.80}(NCS)_2(s) + 2.20L(g) \qquad (I)$$

$$FeL_{1.80}(NCS)_2(s) \xrightarrow{553.2} Fe(NCS)_2(s) + 1.80L(g) \qquad (II)$$

(ii) $\beta_2 = 5.99$ K min^{-1}

$$FeL_4(NCS)_2(s) \xrightarrow{518.6} FeL_{1.54}(NCS)_2(s) + 2.46L(g) \qquad (III)$$

$$FeL_{1.54}(NCS)_2(s) \xrightarrow{601.6} Fe(NCS)_2(s) + 1.54L(g) \qquad (IV)$$

(iii) $\beta_3 = 9.84$ K min^{-1}

$$FeL_4(NCS)_2(s) \xrightarrow{535.2} FeL_{1.40}(NCS)_2(s) + 2.60L(g) \qquad (V)$$

$$FeL_{1.40}(NCS)_2(s) \xrightarrow{605.6} Fe(NCS)_2(s) + 1.40L(g) \qquad (VI)$$

The distribution of the four evolved molecules of ligand between the two decomposition steps changes with the heating rate. This is the reason for presenting separately the results concerning the thermal stability of $FeL_4(NCS)_2$.

TABLE 1

Experimental data for reactions I–VI

Reaction number	T_1 (K)	T_2 (K)	T_3 (K)	T_4 (K)	$t_2 - t_1$ (min)	$t_3 - t_2$ (min)	$t_4 - t_3$ (min)
I	460.8	473.4	488.8	503.4	4.590	5.454	5.256
II	526.9	540.8	553.8	568.5	5.064	4.746	5.306
III	470.9	489.8	510.8	530.3	3.198	3.314	3.232
IV	571.4	585.5	598.7	613.4	2.384	2.325	2.430
V	484.4	510.9	530.4	548.7	2.674	1.977	1.815
VI	578.0	590.8	603.5	615.8	1.407	1.233	1.244

For T_1, $\alpha_1 = 0.10$; for T_2, $\alpha_2 = 0.30$; for T_3, $\alpha_3 = 0.60$; for T_4, $\alpha_4 = 0.90$.

TABLE 2

Non-isothermal kinetic parameters for reactions I–VI

Reaction number	$n^{(0)}$	$E^{(0)}$ (kcal mol^{-1})	$A^{(0)}$ [a] (s^{-1})	$n^{(1)}$	$E^{(1)}$ (kcal mol^{-1})	$A^{(1)}$ [a] (s^{-1})	$n^{(2)}$	$E^{(2)}$ (kcal mol^{-1})	$A^{(2)}$ [a] (s^{-1})
I	0.483	13.20	$7.27.10^{4}$	0.406	12.43	$3.10.10^{4}$	0.410	12.47	$3.25.10^{4}$
II	1.358	42.27	$1.08.10^{16}$	1.084	39.33	$6.13.10^{14}$	1.113	39.64	$8.36.10^{14}$
III	0.735	15.44	$7.81.10^{5}$	0.607	14.54	$2.91.10^{5}$	0.616	14.60	$3.14.10^{5}$
IV	1.097	41.96	$7.69.10^{14}$	0.898	39.49	$8.32.10^{13}$	0.915	39.71	$1.02.10^{14}$
V	0.893	23.33	$1.61.10^{9}$	0.780	23.45	$1.68.10^{9}$	0.789	23.51	$1.79.10^{9}$
VI	1.178	53.24	$1.50.10^{19}$	0.939	49.71	$6.62.10^{17}$	0.963	50.09	$9.23.10^{17}$

[a] The superscript figures give the number of iterations.

The iterative method used to evaluate the non-isothermal kinetic parameters [4] is based on the following relationship

$$\log A + n \log(1 - \alpha_{ik}) - \frac{E}{2.303RT_{ik}} = \log \frac{\alpha_k - \alpha_i}{t_k - t_i} \qquad (1)$$

with $\alpha_{ik} \in (\alpha_i, \alpha_k)$ and $T_{ik} \in (T_i, T_k)$, derived from the "reaction order" model. The method was applied to evaluate the non-isothermal kinetic parameters of the decomposition of $FeL_4(NCS)_2$ for $\alpha \in [0.1, 0.9]$. The necessary experimental data for reactions I–VI are given in Table 1. The values of the non-isothermal kinetic parameters are listed in Table 2.

An inspection of Table 2 shows that two iterations are enough to obtain acceptable values for the non-isothermal kinetic parameters. The results show a subunitary value of the reaction order for the first decomposition step and a value close to unity for the second step. The explanation of the trend to increase shown by the reaction order values for the decomposition of the coordination compounds with lesser amounts of ligand was given elsewhere [5].

To answer the question whether the change with heating rate in the repartition of the evolved ligand molecules between the decomposition steps reflects a certain change in the decomposition mechanism, we have to consider the results obtained at 2.77 and 5.99 K min^{-1} (the data obtained at higher heating rates are presumably more affected by mass and heat transfer phenomena). The results given in Table 2 show that, whatever the amount of ligand evolved in the two decomposition steps for the two heating rates considered, the activation energy values as well as the pre-exponential factor values are quite close. Moreover a certain compensation effect can be seen which determines the closeness of the decomposition rates. Thus in our opinion, in spite of the distribution of the evolved ligand between the decomposition steps, there is no important change of mechanism when the heating rate is changed.

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