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Note

ON THE THERMAL STABILITY OF SOME COORDINATION COMPOUNDS GENERATING MIXED OXIDES WITH PEROVSKITIC STRUCTURE. II

EUGENIA EFTIMIE [1], LUMINIŢA PATRON [2], SILVIA PLOŞTINARU [2], ADRIANA CONŢESCU [2] and E. SEGAL [1]

[1] *Chair of Physical Chemistry and Electrochemical Technology, Polytechnical Institute of Bucharest, Bd. Republicii 13, and* [2] *Centre of Physical Chemistry, ICECHIM-Bucharest, Splaiul Independenţei 202, Bucharest (Romania)*

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In a previous note [1], results concerning non-isothermal kinetics of some mononuclear and polynuclear coordination compounds of lanthanum were presented. Following our research, this note deals with the thermal stability and decomposition non-isothermal kinetics of a mononuclear coordination compound of praseodymium with the chloromandelic anion as well as three polynuclear coordination compounds (PCC) of the pairs: Co–La with the chloromandelic anion, Co–Nd and Co–Pr with the salicylic anion.

EXPERIMENTAL

Powders of: $[Pr(ClMand)_3] \cdot 2H_2O$, $[CoLa(ClMand)_5] \cdot 4H_2O$, $[CoPr(Sal)_4(OH)] \cdot 4H_2O$ and $[CoNd(Sal)_4(OH)] \cdot 4H_2O$ (Sal = salicylic anion; ClMand = chloromandelic anion) were used. The compounds were synthesised and analysed according to methods described elsewhere [2]. To investigate the crystalline state of the powdered substances a Philips PW 1400 X-ray diffractometer with chromium K_α radiation was used. The decomposition curves were recorded with a Paulik–Paulik–Erdey type MOM derivatograph (Q-1500, Budapest) at heating rates between 2.5 and 10 K min^{-1}, in a static air atmosphere.

RESULTS AND DISCUSSION

The X-ray diffractograms of the coordination compounds $[Pr(ClMand)_3] \cdot 2H_2O$ and $[CoLa(ClMand)_5] \cdot 4H_2O$ showed an amorphous structure at ambient temperature.

For the PCC $[CoNd(Sal)_4(OH)] \cdot 4H_2O$ the X-ray diffractogram exhibits the ten peaks shown in Table 1. For $\theta = 15°54'$, using Scherrer's formula [3],

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TABLE 1

Diffraction lines of $[CoNd(Sal)_4(OH)]\cdot 4H_2O$ (θ = Bragg angle, d = interplanar distance)

θ	11°	12°24′	13°03′	15°54′	19°42′	21°36′	23°18′	28°24′	28°54′	34°36′
d (Å)	5.99	5.32	4.89	4.17	3.31	3.11	2.89	2.40	2.36	2.01
Relative intensity	73	64	78	100	64	58	41	32	44	37

TABLE 2

Diffraction lines of $[CoPr(Sal)_4(OH)]\cdot 4H_2O$

θ	13°24′	15°36′	19°48′	21°54′	23°30′	34°30′
d (Å)	4.93	4.25	3.34	3.06	2.87	2.02
Relative intensity	70	90	100	45	50	45

the following value for the mean crystallite size was obtained: l = 58 Å.

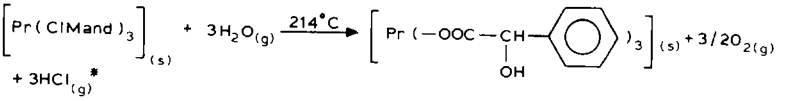
The X-ray diffraction data for the PCC $[CoPr(Sal)_4(OH)]\cdot 4H_2O$ are given in Table 2. For the line with θ = 19°48′ we obtained l = 68 Å.

DECOMPOSITION STEPS AND NON-ISOTHERMAL KINETICS

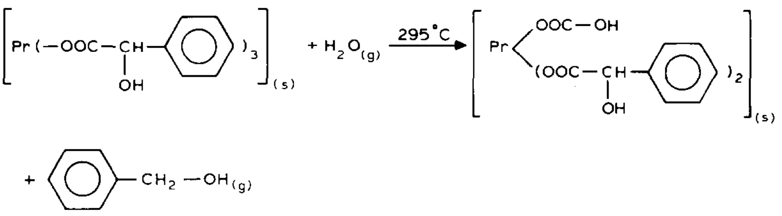
[Pr(ClMand)₃] · 2H₂O

According to the derivatographic data, by progressive heating of $[Pr(ClMand)_3]\cdot 2H_2O$ its thermal decomposition occurs through the following five steps

$$\left[Pr(ClMand)_3\right]\cdot 2H_2O_{(s)} \xrightarrow{120^\circ C} \left[Pr(ClMand)_3\right]_{(s)} + 2H_2O_{(g)} \tag{I}$$



(II)



(III)

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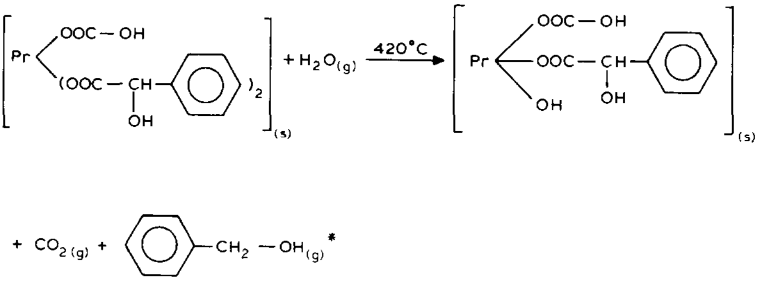
* Besides the water evolved in step I, humidity from the furnace atmosphere should be considered.



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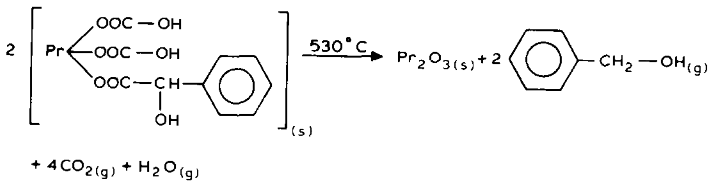

(V)

where the temperature above the arrows correspond to the maximum decomposition rates as given by the DTG curves. As shown by the reactions included in the decomposition sequence the water eliminated in the low-temperature reaction can react with the dehydration product in the following reaction of the sequence which occurs at higher temperature. The values of the non-isothermal kinetic parameters obtained using the Coats–Refern method [4] (reaction order, *n*; activation energy, *E*; and pre-exponential factor, *A*) are given in Table 3.

[CoLa(ClMand)$_5$] · 4H$_2$O

As shown by the derivatographic data obtained at a heating rate of 2.9 K min^{-1}, the decomposition of [CoLa(ClMand)$_5$]·4H$_2$O, occurs according to the following sequence

$$\mathrm{CoLa(ClMand)_5 \cdot 4H_2O_{(s)}} \xrightarrow{70^\circ\mathrm{C}} \mathrm{[CoLa(ClMand)_5]_{(s)} + 4H_2O_{(g)}} \qquad \text{(VI)}$$

TABLE 3

Non-isothermal kinetic parameter values for reactions (I)–(V) [a]

Reaction	I	II	III	IV	V
n	1	1	1	1	1
E (kcal mol^{-1})	12.2	24.3	55	33.5	57.5
A (s^{-1})	7.3×10^4	2.7×10^7	2.6×10^{17}	6.1×10^7	6.7×10^{13}

[a] In Tables 3–6 the data were calculated from the conversion degree, α.

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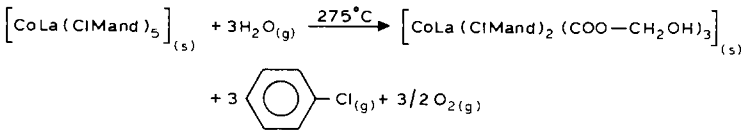
* Or its decomposition products.

TABLE 4

Non-isothermal kinetic parameter values for reactions (VI) and (VII)

Reaction	VI	VII
n	1	1
E (kcal mol^{-1})	10.4	20.1
A (s^{-1})	3.5×10^3	1.8×10^5



(VII)

followed, at higher temperature, by a sequence of overlapping reactions leading to a mixture of cobalt and lanthanum oxides. The values of the non-isothermal kinetic parameters for reactions (VI) and (VII) are listed in Table 4.

[CoPr(Sal)$_4$(OH)] · 4H$_2$O

The recorded derivatograms allowed us to substantiate the following decomposition steps which occur by progressive heating of the powdered samples

$$[\mathrm{CoPr(Sal)_4(OH)}]\cdot 4\mathrm{H_2O_{(s)}} \overset{120^\circ\mathrm{C}}{\rightarrow} [\mathrm{CoPr(Sal)_4(OH)}]\cdot \mathrm{H_2O_{(s)}} + 3\mathrm{H_2O_{(g)}} \quad \text{(VIII)}$$

$$[\mathrm{CoPr(Sal)_4(OH)}]\cdot \mathrm{H_2O_{(s)}} \overset{240^\circ\mathrm{C}}{\rightarrow} [\mathrm{CoPr(Sal)_2O(OH)CO_2}]_{(s)} + 2\mathrm{C_6H_5OH_{(g)}} + \mathrm{CO_{2(g)}} \quad \text{(IX)}$$

$$[\mathrm{CoPr(Sal)_2O(OH)CO_2}]_{(s)} + 4\mathrm{H_2O_{(g)}} \overset{380^\circ\mathrm{C}}{\rightarrow} \mathrm{Co_2O_{3(s)}} + \mathrm{Pr_2O_{3(s)}} + 4\mathrm{C_6H_5OH_{(g)}} + 6\mathrm{CO_{2(g)}} + 5/2\mathrm{H_{2(g)}} \quad \text{(X)}$$

The values of the non-isothermal kinetic parameters for reactions (VIII)–(X) are given in Table 5.

TABLE 5

Non-isothermal kinetic parameter values for reactions (VIII)–(X)

Reaction	VIII	IX	X
n	1	1	2
E (kcal mol^{-1})	11.1	24.7	14.5
A (s^{-1})	9.8×10^3	2.1×10^8	2.7×10^5

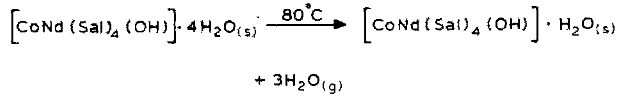
TABLE 6

Non-isothermal kinetic parameter values for reactions (XI)–(XIII)

Reaction	XI	XII	XIII
n	1	1	1
E (kcal mol^{-1})	11.6	26.0	19.6
A (s^{-1})	1.8×10^9	2.7×10^9	1.0×10^6

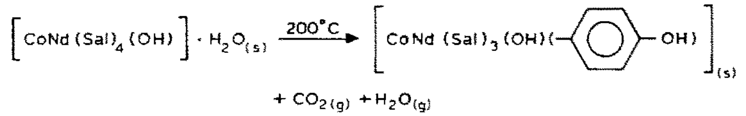
$[CoNd(Sal)_4(OH)] \cdot 4H_2O$

Derivatographic analysis showed the following decomposition steps

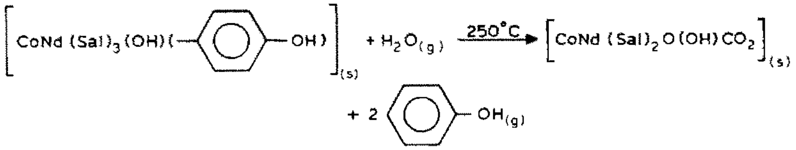


$$[CoNd(Sal)_4(OH)]\cdot 4H_2O_{(s)} \xrightarrow{80^\circ C} [CoNd(Sal)_4(OH)]\cdot H_2O_{(s)} + 3H_2O_{(g)}$$

(XI)



(XII)



(XIII)

At higher temperatures (320–800°C) decomposition continues until a mixture of cobalt and neodymium oxides occurs through a number of overlapping steps. The non-isothermal kinetic parameter values for reactions (XI)–(XIII) are listed in Table 6.

The reported data show that from the 13 reactions analysed from the standpoint of non-isothermal kinetics, only one is characterised by a reaction order value of two. From the 12 reactions with reaction orders of unity, only for reaction (V) does the value of the pre-exponential factor ($A = 6.7 \times 10^{13}$) correspond to that calculated according to the transition state theory [5]. In the other ten cases, the reaction order values are apparent, the decomposition instead being described by a particular form of JMAYK equation for instantaneous nucleation and unidimensional growth of nuclei [6]. In these cases the experimental values of the activation energy equal that for growth. As far as the value $n = 2$ for reaction (X) is concerned, this can be assigned to the reaction of two structural units in the elementary decomposition step.

CONCLUSIONS

(1) An investigation concerning thermal stability and non-isothermal kinetic parameters of the solid–gas decompositions of some mononuclear and polynuclear coordination compounds of La, Pr and Nd was performed.

(2) Most of the decomposition reactions are described by the JMAYK equation.

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