

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

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INTRODUCTION

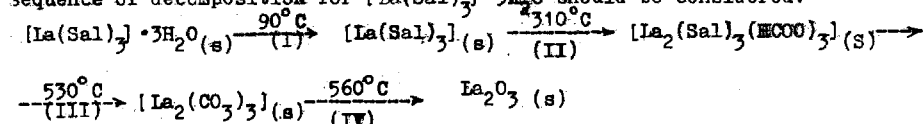
Following our research concerning thermal stability of coordination compounds [1] this note deals with nonisothermal kinetics concerning the solid state decomposition of some mononuclear coordination compounds (m.c.c.) of lanthanum and cobalt and almost polynuclear coordination compounds (p.c.c.) of the pairs La-Co and Nd-Co with salicylic acid and chloromandelic acid. The final product of the thermal decomposition for all the p.c.c. consists of a mixture of oxides, which by a proper subsequent treatment leads to a mixed oxide with perovskitic structure and the general formula ABO_3 , where A=La or Nd and B=Co; such compounds exhibit catalytic properties for oxidation-reduction reaction [2], dehydrogenation [3] as well as for depollution processes which are similar to those exhibited by platinum catalysts.

MEASURING METHODS

The following powdered compounds have been used: $[La(Sal)_3] \cdot 3H_2O$; $[Co(Sal)(OH)] \cdot 4H_2O$; $[CoLa(Sal)_4(OH)] \cdot 4H_2O$; $[CoLa(ClMand)_5] \cdot 4H_2O$; $[CoNd(Sal)_4(OH)] \cdot 4H_2O$, where Sal and ClMand means the salicylic and chloromandelic anions respectively; the heating curves were recorded by help of a MOM Budapest Q1500 derivatograph type Paulik-Paulik-Erdey, at heating rate between 2.5K/min and 10K/min. The cristaline state of the solid compounds has been investigated with a Philips P.W.1400 X-Ray diffractometer using the chromium K α radiation. The values of the kinetic parameters have been obtained by working the derivatographic data using the Coats-Redfern method [4].

RESULTS AND DISCUSSION

The X-Ray diffractograms of all the coordination compounds with La-Co showed an amorphous structure; the p.c.c. which contains Nd-Co exhibits a crystalline structure - the main of crystallites calculated according to Scherrer's formula is $d = 160 \text{ \AA}$. The X-Ray diffraction analysis of the decomposition products of $[\text{La}(\text{Sal})_3] \cdot 3\text{H}_2\text{O}$ between 650°C and 850°C allowed to identify the lanthanum carbonate as well as the lanthanum oxide. The only decomposition product at 950°C is La_2O_3 . Taking account these results, the derivatographic data and the literature information [5], the following sequence of decomposition for $[\text{La}(\text{Sal})_3] \cdot 3\text{H}_2\text{O}$ should be considered:

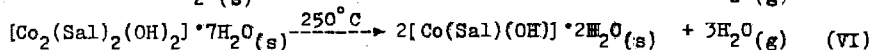
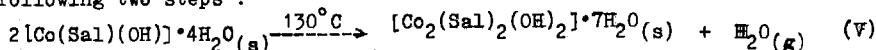


where the temperature above the arrows correspond to the maximum decomposition rates.

The values of the nonisothermal kinetic parameters for reactions (I), (II), (III) are the following:

<u>REACTION (I)</u>	<u>REACTION (II)</u>	<u>REACTION (III)</u>
$n = 1$	$n = 1$	$n = 1$
$E = 10.7 \text{ kcal/mol}$	$E = 15.0 \text{ kcal/mol}$	$E = 3.6 \text{ kcal/mol}$
$A = 1.6 \cdot 10^4 \text{ s}^{-1}$	$A = 1.7 \cdot 10^5 \text{ s}^{-1}$	$A = 4.3 \cdot 10^3 \text{ s}^{-1}$

The dehydration of the m.c.c. $[\text{Co}(\text{Sal})(\text{OH})] \cdot 4\text{H}_2\text{O}$ occurs in the following two steps:



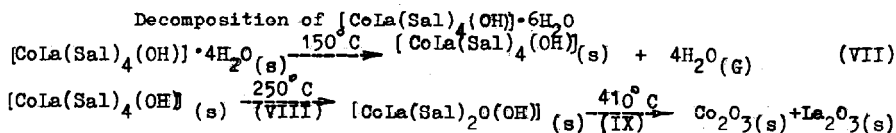
Subsequent heating of the dehydrated compound leads to overlapping decomposition steps which can not be resolved in suitable forms for kinetic analysis as well as to the decomposition of Co_3O_4 to CoO . The following values of the kinetic parameters have been obtained for reaction (V) and (VI):

<u>REACTION (V)</u>	<u>REACTION (VI)</u>
$n = 1$	$n = 1$
$E = 1400 \text{ cal/mol}$	$E = 66 \text{ kcal/mol}$
$A = 1.3 \cdot 10^3 \text{ s}^{-1}$	$A = 1.6 \cdot 10^6 \text{ s}^{-1}$

The low value of the activation energy corresponding to reaction (V) can be assigned to the decomposition of a metastable surface intermediate.

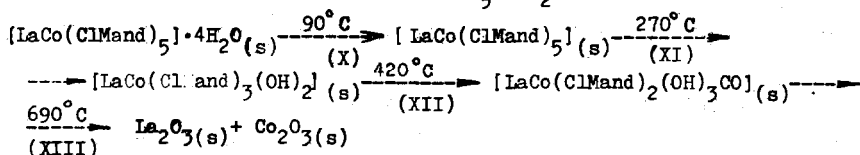
For the other p.c.c. the decomposition sequence and the associated

kinetic parameters are given below :

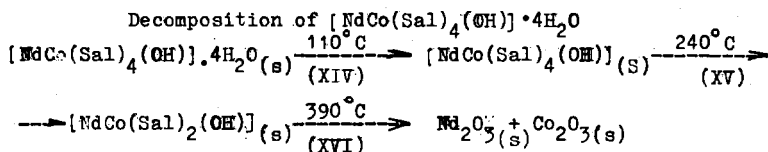


REACTION (VII)	REACTION (VIII)	REACTION (IX)
n = 1	n = 1	n = 2
E = 7.78 kcal/mol	E = 30.1 kcal/mol	E = 52 kcal/mol
A = $3 \cdot 10^3 \text{ s}^{-1}$	A = $4.52 \cdot 10^3 \text{ s}^{-1}$	A = $6.06 \cdot 10^{13} \text{ s}^{-1}$

Decomposition of $[\text{LaCo}(\text{ClMand})_5] \cdot 4\text{H}_2\text{O}$:



REACTION (X)	REACTION (XI)	REACTION (XII)	REACTION (XIII)
n = 1	n = 1	n = 1	n = 1
E = 8.07 kcal/mol	E = 22.43 kcal/mol	E = 25.4 kcal/mol	E = 18.4 kcal/mol
A = $1.12 \cdot 10^2 \text{ s}^{-1}$	A = $3.66 \cdot 10^6 \text{ s}^{-1}$	A = $3.6 \cdot 10^5 \text{ s}^{-1}$	A = $6.8 \cdot 10^3 \text{ s}^{-1}$



REACTION (XIV)	REACTION (XV)	REACTION (XVI)
n = 1	n = 1	n = 1
E = 11.7 kcal/mol	E = 24.1 kcal/mol	E = 29.4 kcal/mol
A = $4.6 \cdot 10^6 \text{ s}^{-1}$	A = $2.8 \cdot 10^{11} \text{ s}^{-1}$	A = $8.9 \cdot 10^{11} \text{ s}^{-1}$

CONCLUSIONS

An analysis of the reported data shows that in almost all the cases the values of the reaction order equal unity. Taking into account the relatively low values of the preexponential factors compared with those predicted by the transition state theory [6] one conclude that reaction order value is an aparent one. Actually a kinetic equation corresponding to a reaction order value which equals unity, is a particular form of the

JMAYK eqn. for instantaneous nucleation and unidimensional growth of the nuclei[7]. For reactions (XV) and (XVI) , the value of the preexponential factor being close to that predicted by the t.s.t., one can suspect a true reaction order $n = 1$. As far as the value $n = 2$ (for reaction IX) is concerned, this could be eventually assigned to the decomposition of two structural units in the elementary step of thermoanalysis.

REFERENCES

- 1 Maria Brezeanu, Eugenia Tatu, Silvia Bolai, Oana Brezeanu, Luminița Patron, E. Segal, *Thermochim. Acta*, 78 (1984) 351
- 2 M. Crespín, W.K.Hall, *J.Catalysis*, 69 (1981) 359
- 3 P.Lombardo, *J.Chem.Soc., Chem.Comm.*, (1980) 467
- 4 A.W.Coats, J.P.Redfern, *Nature*, 20 (1964) 68
- 5 K.Kishore, R.Nagarajan, *J.Thermal Anal.*, 22 (1981) 25
- 6 H.Eyring, S.H.Lin, S.M.Lin, "Basic Chemical Kinetics" (in russian)
MIR, MOSCOW, 1983, p.219
- 7 J.Sestak, "Thermophysical Properties of Solids", Academia PRAHA,
1984, p.190-191