

SOLID STATE KINETIC PARAMETERS OF THE DEHYDRATION OF $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ BY ISOTHERMAL THERMOGRAVIMETRIC MEASUREMENTS

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ABSTRACT

The dehydration of cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was investigated by means of isothermal and non-isothermal TG measurements and non-isothermal DSC measurements. Three processes, corresponding to the successive losses of 4 mol, 1 mol and 1 mol of water have been separated. The ΔH values are 81.5 kJ mol^{-1} , 19.8 kJ mol^{-1} and 98.1 kJ mol^{-1} , respectively; the activation energies are 41.5 kJ mol^{-1} , 91.4 kJ mol^{-1} and 56.5 kJ mol^{-1} , respectively.

Taking into consideration the known structures of the intermediate steps, the E_a values have been analyzed with reference to free space which the water molecule finds when it escapes from the crystal lattice.

INTRODUCTION

Recently, we have investigated the dehydration–anation reactions of several series of aquaammine complexes of transition metals, and in particular Cr(III), Co(III), Rh(III) and Ir(III) [1]. The results have indicated that, in spite of the dissociative mechanism attributed to these processes, the activation energy essentially depends on the entering anion. Perhaps it would be better to say that this energy depends on the structural ratio between cations and anions, that is to say the free space in the crystal from where the water molecule can escape, due to the formation of a non-ionic Frenkel defect according to House theory [2].

We can summarize our previous results as follows: (a) the House theory concerning the importance of the crystal field activation energy (CFAE) is not always accomplished, especially with the second and third row cations

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(e.g., Rh and Ir); (b) neither is this theory accomplished with anions which present special peculiarities, e.g., $[\text{Pt}(\text{CN})_4]^{2-}$ which forms strong Pt–Pt interactions in the crystal lattice, which generally diminishes the activation energy [3]; (c) in a given series of compounds, the volume of the ligands is always the determinant factor. That is to say, the activation energy values are different with ligands such as ethylenediamine, 1,3-diaminopropane, 1,2-diaminopropane or 1,2-diaminocyclohexane [4].

We can summarize all these considerations if we suppose that the determinant step in the dehydration–anation processes is the “free space” in the crystal lattice. Where there is less free space among the ions, the water molecules can occupy an interstitial position only with considerable lattice deformation, so that the activation energy is greater.

To verify this hypothesis, we proposed to carry out a series of experiments on the dehydration–anation reactions of several compounds of the known structure. Moreover, these compounds could have the possibility of several steps before the arrival of the total dehydration. In all the intermediate stages we can compare the partial results with the structure of this intermediate.

The hydrate of cobalt(II) chloride provides a series of reactions as above. In this paper we shall study the dehydration reactions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to CoCl_2 and we investigate the relation between the activation energy and the free space in the crystal lattice.

The thermodynamic aspects of this process have been studied in detail by Grindstaff and Fogel [5] in a previous work, but nothing about the kinetic parameters and their relation to the thermodynamic data has been published.

EXPERIMENTAL

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer TGS-1 system in a nitrogen atmosphere. Non-isothermal measurements were made at a rate of 5°C min^{-1} with 5–7-mg samples. The kinetic parameters were determined on the basis of the general kinetic relation

$$d\alpha/dt = k(T)f(\alpha)$$

where $k(T) = k_0 \exp(-E_a/RT)$ (Arrhenius law); k_0 = frequency factor; E_a = activation energy and α = mole fraction. Mathematically, this expression can be converted to

$$\int_0^1 d\alpha/f(\alpha) = \int_{T_0}^{T_1} k(T) dt \text{ being } d\alpha/f(\alpha) = g(\alpha)$$

TABLE 1
Kinetic functions, $g(\alpha)$, used in their integral form

Mechanism	$g(\alpha)$
<i>Nucleation controlled</i>	
Exponential law	$\ln \alpha^n$
Power law	$\alpha^{1/n}$
<i>Growth controlled</i>	
for $n=1$	$[1-(1-\alpha)^{1-n}]/(1-n)$ $[-\ln(1-\alpha)]$
<i>Nucleation-growth controlled</i>	
Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/n}$
Prout-Tompkins	$\ln[\alpha/(1-\alpha)]$
<i>Diffusion controlled</i>	
One-dimensional	α^2
Two-dimensional	$\alpha + (1-\alpha) \ln(1-\alpha)$
Three-dimensional	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional	$(1-2/3\alpha) - (1-\alpha)^{2/3}$

The main difficulty in solid kinetics is to find the appropriate expressions of $g(\alpha)$ and $f(\alpha)$.

In this work we have used all the principal expressions of $g(\alpha)$ indicated in the literature [6] (Table 1), following the four physical models of solid-state chemistry: nucleation, growth, nucleation-growth and diffusion. The true activation energy was determined by a series of isothermal TG curves which gave a value of E_a almost independent of the physical model proposed [7]. To find the more likely solid-state model this value has been compared with the variable values obtained with non-isothermal measurements. In non-isothermal measurements the expression $g(\alpha) = k(T) dt$ was resolved by the widely employed approximation of Coats and Redfern [8]. For isothermal analysis the general equation is simply $g(\alpha) = kt$. All the calculations were done with a FORTRAN IV program.

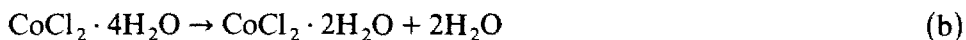
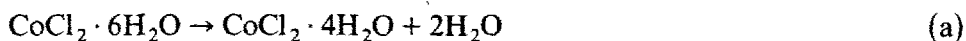
DSC studies

DSC curves were recorded with a Perkin-Elmer DSC-2 with a heating rate of 5°C min^{-1} in a nitrogen atmosphere, with 8–10-mg samples.

RESULTS AND DISCUSSION

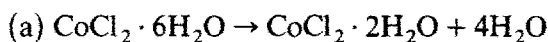
The equilibrium thermal decomposition of the cobalt(II) chloride hydrate was studied through the temperature range 293–473 K. The observed

reactions are in accordance with those proposed in the literature [5]. These reactions can be written as follows



However, in our DSC and TG studies it was impossible to separate the (a) and (b) reactions, because they overlapped very much and all attempts to separate them could lead to a great error in calculating the kinetic parameters.

For this reason, in this work we shall study just three reactions as follows.



In the hexahydrate, two molecules of water are separated from the $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$ inner coordination sphere and are hydrogen bonded, with distances close to that found in ice (O–O distance 2.69 Å in the hydrate and 2.74 Å in ice) [5,9].

The loss of the two crystallization water molecules and two coordination water molecules is practically simultaneous. Besides, according to Grindstaff and Fogel [5] the loss of the second pair of water molecules has the same energy as the loss of the first pair, although the second pair must be from the inner coordination sphere [5]. The probable structure change is that with the loss of the first two water molecules, the $[\text{CoCl}_2(\text{H}_2\text{O})_4]$ molecular units come closer together without altering the structure of the unit cell. We can explain the loss of the next two water molecules if the chloride ions of the two adjacent units of $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$ replace the water molecule in the next units. This produces the square of chloride ions around each cobalt(II) ion and links all the central metal ions into a polymeric structure along the *b*-axis with the chloride ions acting as the linking ions (Fig. 1) [10]. The ΔH of this first process is 81.5 kJ mol^{-1}

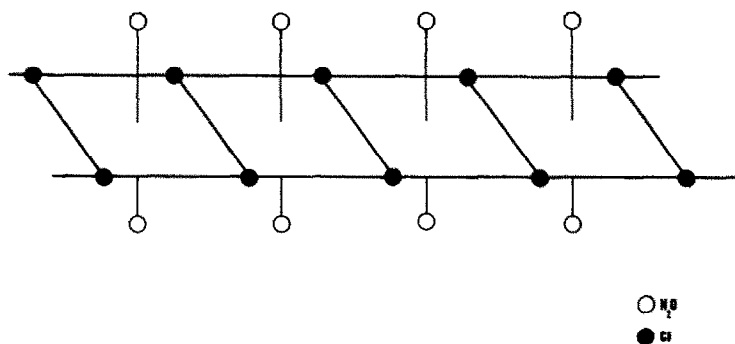


Fig. 1. Idealized structure of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$.

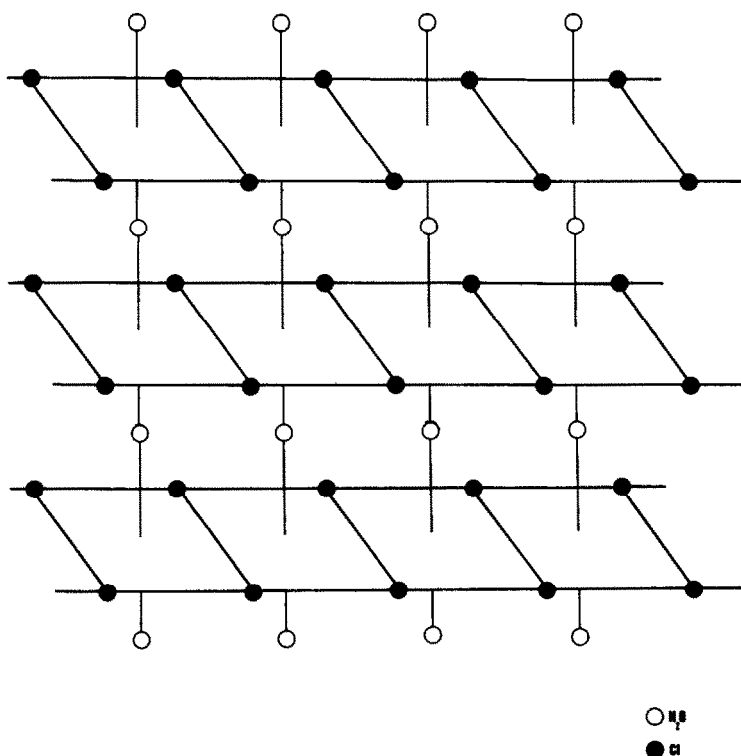
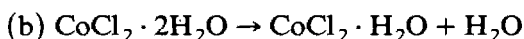


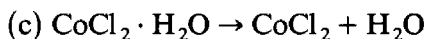
Fig. 2. Idealized structure of $\text{CoCl}_2 \cdot \text{H}_2\text{O}$.

The second reaction studied by DSC and TG is:



The ΔH in this reaction is very low (19.8 kJ mol^{-1}). This can be explained by supposing that in the dihydrate the water molecules in adjacent units are in line with each other and so distant that there is no interaction (Fig. 1).

The third reaction is:



The ΔH for this reaction is very high (98.1 kJ mol^{-1} —almost five times greater than ΔH for the previous reactions). This high value can be understood by taking into account the structures of $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ (Fig. 2) and anhydrous CoCl_2 and the total necessary rearrangement to pass from monohydrated to anhydrous CoCl_2 .

The $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ has a very similar structure to the previous $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, with a difference due to the loss of a molecule of water, which gives a two-dimensional (2-D) structure in which each cobalt(II) is octahedrally surrounded by four shared chlorides and by two shared water molecules (in the *trans* position) (Fig. 2). Finally, the anhydrous CoCl_2 has the typical

and well-known structure of CdCl_2 (two-dimensional with each Cd octahedrally surrounded) [11].

TG measurements

The non-isothermal curve for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is given in Fig. 3. The isothermal curves were obtained at six different temperatures for each process.

In order to calculate the kinetic parameters, all the principal expressions of the solid-state decomposition are used (Table 1) both in isothermal and non-isothermal measurements (see Experimental). The results obtained for the three processes are given in Tables 2–5. The computation for each $g(\alpha)$ and for each n has been carried out with an ad hoc FORTRAN IV program. Taking into account that the similar processes are never described in terms of the diffusion law, we could expect that these processes behave according to the growth, nucleation–growth or nucleation laws. Effectively, the E_a , k_0 and r^2 values found with the diffusion models are inconsistent when comparing the non-isothermal and isothermal measurements. Therefore, only the values found for each compound from the growth, nucleation and nucleation–growth models are reported in Tables 2–4. For brevity, and in order to indicate only the most prominent features, only the kinetic parameters (for a few n values) are given in Tables 2–4 (in fact these parameters were calculated for more n values). It is known from the literature [12,13] that this apparent order, n , is not restricted to being an integer only but may also be a decimal number.

From Tables 2–4 it is evident that the values of E_a and k_0 can be deduced from isothermal curves, since the values thus obtained are almost independent of the physical model proposed, as has been recently pointed out by Criado and co-workers [7].

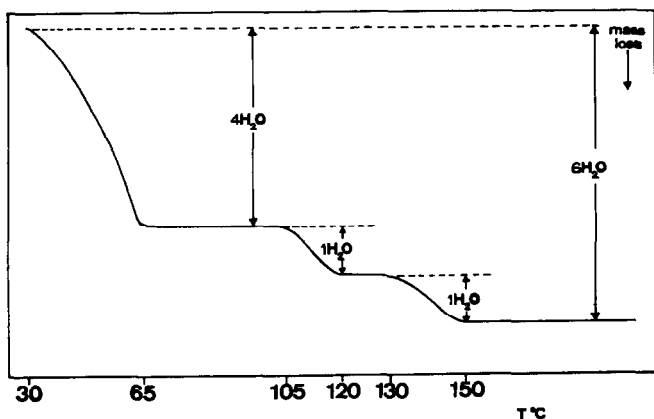


Fig. 3. Non-isothermal TG curve for $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$.

TABLE 2

Selected values of computational kinetic parameters for $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O} \rightarrow \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$

	Growth model		Nucleation-growth model (Avrami-Erofeev)				Nucleation model (power law)		
	$n = 1/2$	2/3	$n = 1$	1.5	2.0	2.5	3.0	$n = 0.5$	1.0
Non-isothermal measurements									
E_a (kJ mol ⁻¹)	66.11	70.80	78.30	50.41	36.46	28.09	22.51	116.34	55.48
$\ln k_0$	21.96	23.83	26.81	16.2	10.78	7.46	5.19	40.17	17.68
r^2	0.9911	0.9932	0.9950	0.9947	0.9943	0.9938	0.9933	0.9842	0.9826
Isothermal measurements									
E_a (kJ mol ⁻¹)	40.89	40.24	39.40	41.48	42.58	43.37	43.92	38.08	42.78
$\ln k_0$	13.67	13.62	13.52	13.95	14.15	14.25	14.30	12.25	13.98
r^2	0.9983	0.9915	0.9984	0.9956	0.9976	0.9954	0.9927	0.9829	0.9928

TABLE 3

Selected values of computational kinetic parameters for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{CoCl}_2 \cdot \text{H}_2\text{O}$

	Growth model		Nucleation-growth model (Avrami-Erofeev)				Nucleation model (power law)		
	$n = 1/2$	2/3	$n = 1$	1.5	2.0	2.5	3.0	$n = 0.5$	1.0
Non-isothermal measurements									
E_a (kJ mol ⁻¹)	201.63	217.57	243.40	160.13	118.49	93.49	76.85	338.57	166.06
$\ln k_0$	60.96	66.07	74.32	48.15	34.97	27.00	21.66	104.48	49.54
r^2	0.9894	0.9930	0.9968	0.9967	0.9966	0.9965	0.9964	0.9775	0.9766
Isothermal measurements									
E_a (kJ mol ⁻¹)	95.57	97.56	100.66	95.64	93.01	91.39	90.30	100.19	90.82
$\ln k_0$	29.07	29.86	31.08	26.89	25.83	27.43	26.93	30.16	27.20
r^2	0.9682	0.9536	0.9280	0.9655	0.9806	0.9876	0.9913	0.9371	0.9928

TABLE 4

Selected values of computational kinetic parameters for $\text{CoCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{CoCl}_2$

	Growth model		Nucleation-growth model (Avrami-Erofeev)			Nucleation model (power law)			
	$n = 1/2$	$2/3$	$n = 1$	1.5	2.0	2.5	3.0	$n = 0.5$	1.0
Non-isothermal measurements									
E_a (kJ mol ⁻¹)	140.75	151.07	167.67	109.48	80.39	62.93	51.29	241.93	117.51
$\ln k_0$	38.50	41.63	46.65	29.52	20.86	15.60	12.06	67.39	31.42
r^2	0.9928	0.9954	0.9980	0.9979	0.9978	0.9977	0.9976	0.9836	0.9826
Isothermal measurements									
E_a (kJ mol ⁻¹)	56.55	58.10	59.30	57.68	57.05	56.73	56.54	57.15	53.33
$\ln k_0$	15.19	15.80	16.40	15.61	15.19	14.91	14.70	14.99	13.85
r^2	0.9682	0.9682	0.9478	0.9674	0.9758	0.9801	0.9827	0.9622	0.9687

TABLE 5

Average kinetic parameters

	ΔH (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)	$\ln k_0$	ΔS^\ddagger (cal mol ⁻¹)	Model
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$	81.5	41.5	13.95	-32.9	Nucl. Growth, $n = 1.5$
$\text{CoCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{CoCl}_2 \cdot \text{H}_2\text{O}$	19.8	91.4	27.43	-6.5	Nucl. Growth, $n = 2.5$
$\text{CoCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{CoCl}_2$	98.1	56.5	14.70	-31.9	Nucl. Growth, $n = 3.0$

The average kinetic parameters E_a and k_0 are given in Table 5. Taking into account the possible deviation and error of these values we can affirm that the activation energies are: $41.5 \pm 2 \text{ kJ mol}^{-1}$ for the first process; $91.4 \pm 3 \text{ kJ mol}^{-1}$ for the second process and $56.5 \pm 2 \text{ kJ mol}^{-1}$ for the third process.

Many investigations, mainly in non-isothermal TG, assume a certain physical model; i.e., a determined $f(\alpha)$ or $g(\alpha)$. In order to avoid assumptions, the solid-state mechanism may be established by comparing the dynamic and isothermal conditions, using an accurate value of r^2 and taking into consideration the shape of the TG isothermal runs, as suggested by other authors [14]. The advantage of this method is that nothing is assumed about the mechanism, but all the kinetic parameters are determined from experimental results.

In the three processes studied here, there is a good agreement with the nucleation–growth model (Avrami law) which also agrees with the sigmoid shape of the isothermal TG curves [6] (Table 5).

The activation energy of the first process is very low, but taking into account that this corresponds to the loss of two different water molecules it is very difficult to interpret this result. The loss of the first two water molecules leaves the lattice structure relatively unaffected [5]; the loss of the second pair of water molecules (coordination water) is very easy because the structure is “open” due to the simultaneous loss of crystallization water. Therefore there is a relatively large free space which greatly facilitates the escape of these water molecules.

In the second process, the loss of the water from the dihydrate presents a relatively high activation energy (ca. 90 kJ mol^{-1}). It is a process in which one of the water molecules (coordination water) is lost to give a two-dimensional structure in which the chlorides and water molecules are shared. The free space between each chain (dihydrate) is small and very much hindered by the strong hydrogen bonding between the coordinated water and the leaving water.

On the other hand, to pass from $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ to CoCl_2 there is a great rearrangement in the structure, which is open, leaving many tunnels which allow the easy escape of the water molecule. The activation energy must be low (Table 5) but the ΔH must be very great, due to this rearrangement. In reality, ΔH is approximately 100 kJ mol^{-1} , while in the previous process, without rearrangement it is approximately only 20 kJ mol^{-1} .

Furthermore, the entropy of activation calculated from the expression

$$(\ln K)h/(k_bT) = \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

where K is the rate constant, also may indicate the differences between the steps of the dehydration (Table 5). According to House [2] the entropy effect may also be explained by the relative sizes (in our case the relative packing) of the ions and the free volume: where there is a large space between the

ions (as we suppose in the first and third steps) the water molecule may be able to slip into an interstitial position causing little or no lattice distortion. Therefore the entropy of activation may be negative. Where there is a smaller space between the ions (as we can suppose in the second step), the water molecules can occupy an interstitial position only with considerable lattice expansion so that the entropy of activation is less negative or even positive (Table 5). Although this entropy reasoning of House is speculative and not supported by any facts, we believe that it gives an intuitive comprehension of the process.

CONCLUSION

The energetic diagram of the dehydration-anation of the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ can be represented as follows:

This diagram explains that the most stable species is $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. In the TG curves (Fig. 1) we may clearly see this fact: it is the species which exists in the greatest temperature interval. On the other hand, once the activation energy for the monohydrate is surpassed, $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ and CoCl_2 are formed rapidly and their temperature interval is very low.

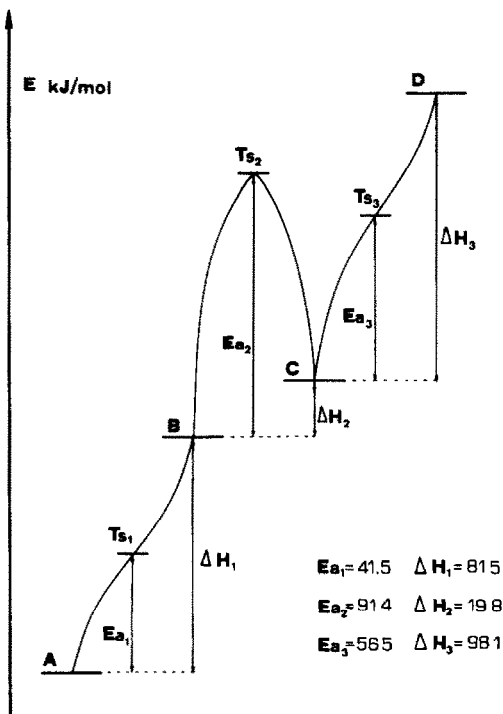


Fig. 4. Energetic diagram for the dehydration of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

ACKNOWLEDGMENTS

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REFERENCES

- 1 (a) M. Serra, A. Escuer, J. Ribas, M.D. Baró and J. Casabó, *Thermochim. Acta*, 56 (1982) 183; (b) M. Serra, A. Escuer, J. Ribas and M.D. Baró, *Thermochim. Acta*, 64 (1983) 237; (c) M. Monfort, M. Serra, A. Escuer and J. Ribas, *Thermochim. Acta*, 69 (1983) 397; (d) M. Corbella, C. Diaz, A. Escuer, A. Seguí and J. Ribas, *Thermochim. Acta*, 74 (1984) 23; (e) J. Ribas, M. Serra and A. Escuer, *Inorg. Chem.*, 23 (1984) 2236; (f) M. Serra, A. Escuer and J. Ribas, *Thermochim. Acta*, 80 (1984) 103; (g) J. Ribas, A. Escuer and M. Monfort, *Inorg. Chem.*, 24 (1985) 1874.
- 2 J.E. House, Jr., *Thermochim. Acta*, 38 (1980) 59.
- 3 See ref. 1(e) and references therein.
- 4 M. Corbella and J. Ribas, *Inorg. Chem.*, accepted.
- 5 W.K. Grindstaff and N. Fogel, *J. Chem. Soc., Dalton Trans.*, (1972) 1477.
- 6 C.H. Bamford and C.F.H. Tipper (Eds.), *Comprehensive Chemical Kinetics*, Vol. 22; *Reactions in the Solid State*, Elsevier, Amsterdam, 1980, Ch. 3.
- 7 J.M. Criado, M. Gonzales, A. Ortega and C. Real, *J. Therm. Anal.*, 29 (1984) 243.
- 8 A.W. Coats and J.P. Redfern, *Nature (London)*, 201 (1964) 68.
- 9 J. Mizuno, *J. Phys. Soc. Jpn.*, 15 (1960) 1412.
- 10 B. Morosin and E.J. Graeber, *Acta Crystallogr.*, 16 (1963) 1176.
- 11 H. Grime and J.A. Santos, *Z. Kristallogr.*, 88 (1934) 136.
- 12 D. Blečić and Z.D. Živković, *Thermochim. Acta*, 60 (1983) 68.
- 13 A.C. Norris, M.I. Pope and M. Selwood, *Thermochim. Acta*, 41 (1980) 357.
- 14 See ref. 6 and T.B. Tang and M.N. Chandri, *J. Therm. Anal.*, 18 (1980) 247.