Thermochimica Acta, 69 (1983) 397–407
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

KINETIC PARAMETERS AND SOLID STATE MECHANISM OF THE THERMAL DEHYDRATION OF *trans*$[CrF(H_2O)(aa')_2]K[Cr(CN)_6]H_2O$ AND *trans*$[CrF(H_2O)(aa')_2]K[CrNO(CN)_5]H_2O$ (aa′ = ETHYLENEDIAMINE OR 1,3-DIAMINOPROPANE)

M. MONFORT, M. SERRA, A. ESCUER and J. RIBAS *

Departament de Quimica Inorgánica, Facultat de Quimica, Universitat de Barcelona, Barcelona (Spain)

(Received 25 May 1983)

ABSTRACT

The solid phase thermal deaquation of *trans*$[CrF(H_2O)(aa')_2]K[Cr(CN)_6]H_2O$ and *trans*$[CrF(H_2O)(aa')_2]K[CrNO(CN)_5]H_2O$ (aa′ = ethylenediamine or 1,3-diaminopropane) has been investigated by means of TG measurements. The kinetic parameters (activation energy, E_a, activation entropy, $\Delta S^{\#}$, and frequency factor, k_0) have been determined by comparison of the isothermal and non-isothermal studies for all the principal $g(\alpha)$ expressions. The values found for the activation energy are low (between 80 and 110 kJ $mole^{-1}$, approximately) and permit the assignment of the deaquation–anation mechanism of the S_N1 type, involving square-pyramid activated complex and elimination of water as Frenkel defects.

INTRODUCTION

The solid phase deaquation–anation of aquopentamminemetal(III) salts

$$[M(H_2O)(NH_3)_5]X_3(s) \rightarrow [M(X)(NH_3)_5]X_2(s) + H_2O(g)$$

where M = Co(III), Cr(III), Ru(III) and Rh(III), has been studied by several authors since 1959, notably by Wendlandt et al. [1–6], Tsuchiya et al. [7–9] and others [10]. The activation energies for these reactions are reported to vary with the anion. This apparent anion effect has been attributed to an S_N2 (or associative mechanism) ligand exchange between the departing H_2O and the entering anion, X. However, for the same substances, the activation parameters reported by different researchers are in poor agreement. According to Lemay [11], this is due to the fact that the experimental conditions have not been specified or controlled. Thus, as Lemay points out, when

---

* To whom correspondence should be addressed.

0040-6031/83/$03.00

procedural variables are held constant, activation parameters for different salts agree within experimental error. This could mean, according to the House theory [12], that an S_N1 (dissociative) mechanism is involved in the ligand exchange process rather than an S_N2.

On the other hand, we think that, in addition to the experimental procedures, it is necessary to specify whether the method used to calculate the kinetic parameters is isothermal or non-isothermal. In any case, the criterion followed to choose the appropriate $g(\alpha)$ expression must be clear. In our work on the amine complexes of chromium(III), we have seen, according to the literature [13,14], that it is very difficult, if not impossible, to find both the accurate value of the activation energy and the possible mechanism from non-isothermal TG curves only. In all cases, at least one isothermal curve is necessary. In any case, the more real activation energy is best determined by a series of isothermal TG curves which gives an activation energy value, E_a, almost independent of the physical model proposed (nucleation, growth, diffusion or intermediates). In this procedure, one non-isothermal curve is necessary to determine the best solid mechanism state (not always unambiguously). Taking into account this procedure, if we assume an S_N1 mechanism, explained in terms of Frenkel defect formation by elimination of water molecules [12], the activation energy must be almost independent of the entering anion and relatively small. On the other hand, according to the difference between the size of the cation and anion, the water molecule may be more or less able to slip into an interstitial position and to escape from the crystal. For this reason, and following our studies on cyano-complexes as entering ligands [15–19], we think that the study of the anation of *trans*$[CrF(H_2O)(aa')_2]^{2+}$ cations (aa′ = en or tmd) with two anions very similar in size, e.g. $[Cr(CN)_6]^{3-}$ and $[CrNO(CN)_5]^{3-}$, would be interesting. The two cations present the possibility of structural differences originated by the greater volume of the tmd(1,3-diaminopropane) ligand. For this reason, we could expect a higher activation energy value for en than for tmd.

In this paper, we describe the results achieved with both isothermal and non-isothermal experiments on the new complexes; we propose a chemical kinetic mechanism and we compare the results with those described by us [18,19] for *trans*$[CrF(H_2O)(tmd)_2][M(CN)_4]$(M=Ni, Pd, Pt).

EXPERIMENTAL

Preparation of the new compounds

The new salts *trans*$[CrF(H_2O)(en)_2]K[Cr(CN)_6]H_2O$, *trans*$[CrF(H_2O)(en)_2]K[CrNO(CN)_5]H_2O$, *trans*$[CrF(H_2O)(tmd)_2]K[Cr(CN)_6]H_2O$ and *trans*$[CrF(H_2O)(tmd)_2]K[CrNO(CN)_5]H_2O$ have been synthesized following the method previously described [17] to prepare the analogous compounds *trans*[CrF(H_2O)(aa$'$)$_2$]K[Co(CN)$_6$]H_2O (aa$'$ = en or tmd). The analyses for Cr, C, N, and H agree with the formulae proposed. Previous TG curves also indicate one mole of water of crystallization per molecule.

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer model TGS-1 system at a rate of 5° min^{-1} in a nitrogen atmosphere (non-isothermal measurements). The amount of sample was 6–7 mg. The kinetic parameters were determined on the basis of the general kinetic relation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\mathrm{f}(\alpha)$$

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

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

The main difficulty in solid kinetics is to find the appropriate expression of g(α) or f(α).

In this work, we have used all the principal expressions of g(α) indicated in the literature [20], following the four physical models of solid state chemistry: nucleation, growth, nucleation–growth and diffusion. To find the real kinetic parameters, we have compared the variable values obtained for non-isothermal measurements with the almost constant values for any model in the isothermal measurements. In the non-isothermal measurements, the expression

$$\mathrm{g}(\alpha) = \int_{T_0}^{T_1} k(T)\mathrm{d}t$$

was resolved by the widely employed approximation of Coats and Redfern [21]. For the isothermal analysis, the general equation is simply $\mathrm{g}(\alpha) = kt$. In this case, isothermal preheating at low temperature (50–60°C) was carried out until weight stabilization.

RESULTS AND DISCUSSION

The non-isothermal TG curves for the solid phase thermal deaquation of *trans*[CrF(H_2O)(en)$_2$]K[Cr(CN)$_6$]H_2O is given in Fig. 1. The TG curves for the three other compounds are very similar, except for slight variations in the starting and final temperatures. A mass loss of approximately 18 a.m.u. occurred between room temperature and 100°C, corresponding to the water

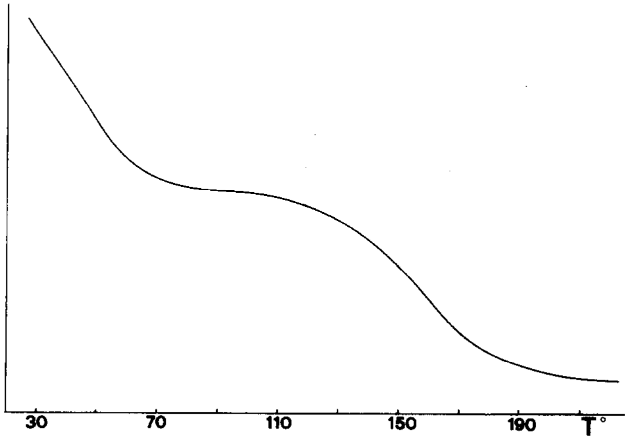

Fig. 1. TG curve of *trans*[$CrF(H_2O)(en)_2$]K[$Cr(CN)_6$]H_2O.

of crystallization. Effectively, if we stop the process at 80–90°C or if we preheat isothermally (50–60°C) to constant weight, the compound so obtained has the same UV-visible and IR spectra as the starting material.

Between 100° and 200°C, there is a second mass loss corresponding to a molecular weight decrease of 18 a.m.u. and a new compound is obtained at

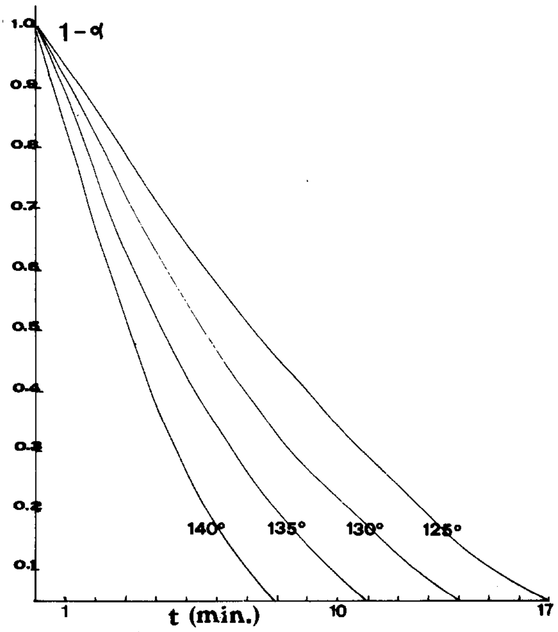

Fig. 2. Isothermal TG curves for *trans*[$CrF(H_2O)(en)_2$]K[$CrNO(CN)_5$]. The curves are cut at $\alpha = 0.05$ in order not to lengthen the abscissa (to arrive at $\alpha = 0$, a time of approximately 40 min may be required for the 125°C curve).

the end of the peak, which corresponds to $K[(en)_2FCr{-}NC{-}Cr(CN)_5]$ according to spectroscopic and magnetic measurements [22]. The isothermal TG curves were determined at four different temperatures for each product. The results for *trans*$[CrF(H_2O)(en)_2]K[CrNO(CN)_5]$ (preheated isothermally at 40°C to constant weight to eliminate the water of crystallization) are given in Fig. 2. The isothermal runs for the other three products are very similar and are not indicated here.

In order to calculate the kinetic parameters, all the principal expressions of the solid state decompositions are used (Table 1). Decomposition reactions of solids are characterized by the so-called "apparent reaction order, n", which is different from the reaction order for homogeneous reactions. It is known from the literature [23,24] that the apparent order does not have to be an integer; it may also be a decimal number. It is only determined by complete agreement of the experimental data with the reaction rate equation. The expressions for $g(\alpha)$ indicated in Table 1 are used both in isothermal and non-isothermal measurements. In order to find the real kinetic parameters, we have employed a combination of isothermal and non-isothermal methods [14,25].

Many investigations made so far over all with non-isothermal methods, accept or assume the reaction mechanism, i.e. the function $g(\alpha)$ or $f(\alpha)$. In order to avoid assumptions, we consider that the reaction mechanism may be established by comparing the dynamic and isothermal conditions, as also suggested by other authors [26,27]. The advantage of this method is the fact that one does not assume the mechanism and the order of reaction, but all kinetic parameters are determined from experimental results.

The results obtained for the new compounds are given in Tables 2 and 3. 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 all the dehydration–anation processes of amine complexes of chromium(III) are described

TABLE 1

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

Mechanism	$g(\alpha)$
Nucleation controlled	$\ln\alpha^n$ $\alpha^{1/n}$
Growth controlled	$[1-(1-\alpha)^{1/n}]/(1-n)$
Nucleation–growth controlled	
Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/n}$
Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$
Diffusion controlled	
One-dimensional	α^2
Two-dimensional	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-dimensional	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional	$(1-2/3\alpha)-(1-\alpha)^{2/3}$

TABLE 2

Computational kinetic parameters for *trans*[$CrF(H_2O)(en)_2$]K[$Cr(CN)_6$] and *trans*[$CrF(H_2O)(en)_2$]K[$CrNO(CN)_5$] using the equations for growth and nucleation–growth mechanisms

	Growth model			
	$n = 0$	$n = 0.3$	$n = 0.5$	$n = 0.7$
trans[$CrF(H_2O)(en)_2$]K[$Cr(CN)_6$]				
E_a (kJ mole^{-1}) [a]	121.55	121.64	121.60	121.45
k_0	0.85×10^{14}	0.11×10^{15}	0.13×10^{15}	0.15×10^{15}
r^2	0.9719	0.9741	0.9756	0.9772
E_a (kJ mole^{-1}) [b]	88.81	99.78	107.71	116.14
k_0	0.16×10^{9}	0.43×10^{10}	0.46×10^{11}	0.57×10^{12}
r^2	0.9825	0.9885	0.9915	0.9939
trans[$CrF(H_2O)(en)_2$]K[$CrNO(CN)_5$]				
E_a (kJ mole^{-1}) [a]	95.57	96.16	96.63	97.14
k_0	0.22×10^{12}	0.34×10^{12}	0.46×10^{12}	0.64×10^{12}
r^2	0.9597	0.9716	0.9780	0.9833
E_a (kJ mole^{-1}) [b]	75.00	83.29	89.21	95.47
k_0	0.90×10^{7}	0.13×10^{9}	0.84×10^{9}	0.62×10^{10}
r^2	0.9978	0.9993	0.9995	0.9993

[a] Isothermal measurements.

[b] Non-isothermal measurements.

in terms of a growth or nucleation–growth model (nucleation and diffusion are never found), we could expect that these new compounds behave according to the same law. Effectively, the values of E_a, k_0 and r^2 found by us with diffusion or nucleation models are inconsistent, over all comparing the non-isothermal and isothermal measurements [28]. For these reasons, in Tables 2 and 3 only the values found for each compound from the growth and nucleation–growth models are reported. In order not to lengthen and to indicate only the more prominent features, in each table are given only the kinetic parameters for $n = 0$, 0.3, 0.5, 0.7, and 1.0 for the growth law (in fact, we have calculated these parameters for $n = 0$, 0.1, 0.2, etc. up to 1.0 and 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0) [28]. The physical model is assigned and the real kinetic parameters are calculated on the basis of agreement in the activation energies, frequency factor and r^2 values in both non-isothermal and isothermal methods (the apparent order, n, can remain, however, ambiguous, but it

Nucleation–growth model			
Avrami–Erofeev			Prout
$n=1$	$n=2$	$n=3$	
121.32	120.95	120.65	120.19
0.18×10^{15}	0.94×10^{14}	0.60×10^{14}	0.25×10^{15}
0.9797	0.9753	0.9739	0.9743
129.73	61.31	38.51	
0.33×10^{14}	0.84×10^{5}	0.92×10^{2}	
0.9962	0.9957	0.9951	
97.99	96.84	96.57	96.95
0.11×10^{13}	0.42×10^{12}	0.27×10^{12}	0.15×10^{13}
0.9893	0.9684	0.9568	0.9522
105.47	49.36	30.67	
0.15×10^{12}	0.53×10^{4}	0.14×10^{2}	
0.9980	0.9978	0.9975	

is not important at all). Furthermore, we have calculated the entropy of activation from the known expression

$$\ln k\left(\frac{h}{K_b}\right)T=\frac{\Delta S^{\#}}{T}-\frac{\Delta H^{\#}}{RT}$$

The kinetic parameters E_a, $\Delta S^{\#}$ and k_0 are given in Table 4. Taking into account the possible deviation and error of these values, we can affirm that the real activation energy of the tmd complexes is somewhat lower than for en complexes (Table 4); the difference between $[Cr(CN)_6]^{3-}$ and $[CrNO(CN)_5]^{3-}$ is also indicated.

The values of k_0 indicate the rigidity of the activated complex (see below). According to Cordes [29] and Shannon [30], the frequency factor is related to the degrees of freedom of the activated complex and may vary between 10^5 and 10^{18} approximately. Small values often indicate a rigid activated com-

TABLE 3

Computational kinetic parameters for *trans*[CrF(H_2O)(tmd)$_2$]K[Cr(CN)$_6$] and *trans*[CrF(H_2O)(tmd)$_2$]K[CrNO(CN)$_5$] using the equations for growth and nucleation–growth mechanisms

	Growth model			
	$n = 0$	$n = 0.3$	$n = 0.5$	$n = 0.7$
trans[CrF(H_2O)(tmd)$_2$]K[Cr(CN)$_6$]				
E_a(kJ mole^{-1})[a]	80.85	83.07	84.50	85.88
k_0	0.37×10^{10}	0.96×10^{10}	0.18×10^{11}	0.33×10^{11}
r^2	0.9999	1.0000	1.0000	1.0000
E_a(kJ mole^{-1})[b]	64.23	72.81	79.03	85.67
k_0	0.38×10^{6}	0.62×10^{7}	0.46×10^{8}	0.39×10^{9}
r^2	0.9816	0.9892	0.9928	0.9955
trans[CrF(H_2O)(tmd)$_2$]K[CrNO(CN)$_5$]				
E_a(kJ mole^{-1})[a]	73.03	74.85	76.17	77.66
k_0	0.98×10^{9}	0.21×10^{10}	0.37×10^{10}	0.70×10^{10}
r^2	0.9547	0.9788	0.9898	0.9966
E_a(kJ mole^{-1})[b]	69.89	77.88	83.61	89.66
k_0	0.51×10^{7}	0.74×10^{8}	0.50×10^{9}	0.37×10^{10}
r^2	0.9986	0.9975	0.9962	0.9943

[a] Isothermal measurements.

[b] Non-isothermal measurements.

plex without degrees of freedom and high values indicate a flexible activated complex. The four present cases (Table 4) are intermediate (10^{10}–10^{13}) and very similar.

Comparing the activation energy data with the other previously reported by us in the series *trans*[CrF(H_2O)(tmd)$_2$][M(CN)$_4$] (M = Ni, Pd, Pt) [18,19] ($E_a \approx 110 \pm 10$ kJ mole^{-1}), we see that the two new tmd compounds have lower activation energy ($\approx 80 \pm 5$ kJ mole^{-1}).

TABLE 4

Average kinetic parameters calculated from the correspondence on isothermal and non-isothermal measurements

See text for the model proposed.

Compound	E_a (kJ mole^{-1})	k_0	$\Delta S^{\#}$ (cal mole^{-1})
trans[CrF(H_2O)(en)$_2$]K[Cr(CN)$_6$]	118.8 ± 6	0.75×10^{13}	3.6 ± 9
trans[CrF(H_2O)(en)$_2$]K[CrNO(CN)$_5$]	96.3 ± 1	0.32×10^{12}	-7.1 ± 8
trans[CrF(H_2O)(tmd)$_2$]K[Cr(CN)$_6$]	85.8 ± 1	0.16×10^{10}	-14.7 ± 10
trans[CrF(H_2O)(tmd)$_2$]K[CrNO(CN)$_5$]	79.9 ± 3	0.21×10^{10}	-17.3 ± 9

Nucleation–growth model			
Avrami–Erofeev			Prout
$n=1$	$n=2$	$n=3$	
87.89	83.49	81.81	81.75
0.82×10^{11}	0.11×10^{11}	0.46×10^{10}	0.22×10^{11}
0.9999	1.0000	0.9998	0.9998
96.43	44.86	26.67	
0.12×10^{11}	0.15×10^{4}	0.57×10^{1}	
0.9978	0.9974	0.9970	
80.14	76.14	74.91	75.40
0.19×10^{11}	0.31×10^{10}	0.15×10^{10}	0.84×10^{10}
1.0000	0.9810	0.9630	0.9608
99.37	46.46	28.83	
0.93×10^{11}	0.43×10^{4}	0.12×10^{2}	
0.9906	0.9894	0.9879	

MECHANISM

House [12] has recently proposed several mechanisms for the thermal dehydration reaction of solid complexes, determined by various types of defects: Schottky defects with an S_N2 associative mechanism, or Frenkel defects with an S_N1 dissociative mechanism. According to this theory, high values of E_a have a better correspondence to an S_N2 mechanism, while low values have a better correspondence to S_N1. In our case, in an S_N2 reaction, the formation of a seven-bond complex (pentagonal bipyramid) based on crystal field model requires 4.26 *Dq* [31], *Dq* being about 25 kJ mole^{-1} for the aquoamine complexes of chromium(III), which alone would be about 105 kJ mole^{-1} greater than the E_a found in at least three cases (Table 4). If the activated complex is octahedrally wedge, the energy required is only 1.8 *Dq* (nearly 50 kJ mole^{-1}). However, considering that, in the S_N2 reaction, heptacoordination suggests a Schottky defect formation in an ionic crystal, it requires high energy ($E_{\mathrm{Sch.}} = 0.35\ U$, U being the lattice energy) [32]. Consequently, we would find a value greater than 120 kJ mole^{-1}.

It is likely, therefore, that we have an S_N1 (dissociative mechanism) with the formation of a square pyramid activated complex, requiring only 2 *Dq*

[31] (activation energy about 50 kJ $mole^{-1}$) (for a trigonal bipyramid activated complex it would require 5.7 *Dq*, i.e. 145 kJ $mole^{-1}$ greater than the E_a found). Consequently, the transition state is determined by the water loss and a non-ionic Frenkel defect formation. This implies no great variation of activation energy regarding one cation and similar anions, in which, a priori, the mechanism would be identical. The marked difference between the activation energy of *trans*$[CrF(H_2O)(en)_2]^{2+}$ and *trans*$[CrF(H_2O)(tmd)_2]^{2+}$ (Table 4) is also a proof of the dissociative mechanism, the water loss being the more important step of the reaction. The water will be able to escape into the interstitial sites of the lattice when the free space in the net is greater. It is evident that we can expect that the free space will be greater with the more voluminous 1,3-diaminopropane ligand than with the ethylenediamine ligand. For this reason, the activation energy of complexes with tmd is lower than those with en.

Furthermore, the entropy of activation also indicates this significative difference between the complexes with en and tmd ligands (Table 4). This entropy is more negative for the tmd complexes. According to House [12], the entropy effect may also be explained by the relative sizes (or relative packing) of the ions and the free volume: where there is a larger space between the cation and anion (as we can expect with the tmd ligand) the water molecule may be able to slip into an interstitial position causing little or no lattice distortion. Therefore, $\Delta S^{\#}$ may be negative. Where there is a smaller space between them (as we can expect for the en ligand), the water molecule can occupy an interstitial position only with great lattice expansion so that the entropy of activation is positive.

For all these reasons, we can conclude that the mechanism of these dehydration–anation reactions may be considered as dissociative (S_N1), with a square pyramid activated complex and an activation energy of approximately 80–120 kJ $mole^{-1}$.

ACKNOWLEDGEMENTS

We are very grateful for the financial support of Fondo Nacional para el Desarrollo de la Investigación Cientifica. Comisión Asesora, 1981.

REFERENCES

1 W.W. Wendlandt and J.L. Bear, J. Phys. Chem., 65 (1961) 1516.
2 J.P. Smith and W.W. Wendlandt, Nature (London), 201 (1964) 291.
3 W.W. Wendlandt, G. D'Ascenzo and R.H. Gore, J. Inorg. Nucl. Chem., 32 (1970) 3404.
4 R.H. Gore and W.W. Wendlandt, Thermochim. Acta, 1 (1970) 491.
5 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition Metal Ammine Complexes, Elsevier, Amsterdam, 1967.

6 W.W. Wendlandt and J.L. Bear, J. Inorg. Nucl. Chem., 22 (1961) 77.
7 M. Mori and R. Tsuchiya, Bull. Chem. Soc. Jpn., 33 (1960) 841.
8 M. Mori, R. Tsuchiya, S. Takemura and E. Matsuda, Bull. Chem. Soc. Jpn., 34 (1961) 1757.
9 R. Tsuchiya, Y. Koji, A. Uehara and E. Kyuno, Bull. Chem. Soc. Jpn., 42 (1969) 1881.
10 A. Ohyoshi, S. Hieraki, T. Odate, S. Kohata and J. Oda, Bull. Chem. Soc. Jpn., 48 (1975) 262.
11 H.E. Lemay and M.W. Babich, Thermochim. Acta, 48 (1981) 147.
12 J.E. House, Jr., Thermochim. Acta, 38 (1980) 59.
13 J. Zsakò, J. Therm. Anal., 5 (1974) 239.
14 J.M. Criado, J. Morales and V. Rives, J. Therm. Anal., 14 (1978) 221.
15 J. Ribas, J. Casabó, M. Serra and J.M. Coronas, Inorg. Chim. Acta, 36 (1979) 41.
16 J. Ribas, M. Serra, A. Escuer and J.M. Coronas, J. Inorg. Nucl. Chem., 43 (1981) 3113.
17 M. Corbella, M. Serra, A. Escuer and J.M. Coronas, J. Inorg. Nucl. Chem., 57 (1982) 283.
18 M. Serra, A. Escuer, J. Ribas, M.D. Baró and J. Casabó, Thermochim. Acta, 56 (1982) 183.
19 M. Serra, A. Escuer, J. Ribas and M.D. Baró, Thermochim. Acta, 64 (1983) 237.
20 M.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
21 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
22 J. Ribas, M. Monfort and J. Casabó, unpublished results.
23 D. Blecic and Z.D. Zivkovic, Thermochim. Acta, 60 (1983) 68.
24 A.C. Norris, M.I. Pope and M. Selwood, Thermochim. Acta, 41 (1980) 357.
25 D. Blecic, Z.D. Zivkovic and M. Martinovic, Thermochim. Acta, 60 (1983) 61.
26 T.B. Tang and M.N. Chaudhri, J. Therm. Anal., 18 (1980) 247.
27 B.N. Achar, G.W. Brindley and H. Sharp, Proc. Int. Clay Conf. Jerusalem, 1, 1966, p. 67.
28 All these values can be obtained on request from the authors.
29 H.F. Cordes, J. Phys. Chem., 72 (1968) 2135.
30 R.B. Shannon, Trans. Faraday Soc., 60 (1964) 1902.
31 F. Basolo, Mechanism of Inorganic Reactions, Wiley, New York, 2nd edn. 1967, p. 67.
32 H. Schmalzreid, Solid State Reactions, Verlag-Chemie, Weinheim, 1974, p. 25.