

## Controlled decomposition rate thermal analysis of $\text{Mg}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ . Kinetic study

Y. Laureiro, A. Jerez, C. Pico and M.L. Veiga \*

*Departamento de Química Inorgánica I, Facultad de Químicas, Universidad Complutense, 28040 Madrid (Spain)*

(Received 26 September 1990)

### Abstract

Thermal decomposition reactions in vacuum of brucite,  $\text{Mg}(\text{OH})_2$ , and the isostructural hydroxide  $\beta\text{-Cd}(\text{OH})_2$  were studied by means of controlled decomposition rate thermal analysis. Kinetic equations governing these processes were determined and the corresponding kinetic parameters were calculated.

### INTRODUCTION

Controlled decomposition rate thermal analysis (CDRTA) is a technique established by Rouquerol [1] in which the heating rate is controlled by means of a signal proceeding from the sample in such a way that the decomposition rate is maintained constant. Temperature is plotted versus time, i.e. versus mass variation, taking into account that the decomposition rate is constant,  $dm/dt = K$  and, then,  $\Delta m = kt$ .

Thermal decompositions in air of brucite,  $\text{Mg}(\text{OH})_2$ , and of the isotype  $\beta\text{-Cd}(\text{OH})_2$  to form the corresponding oxides have been studied by several authors [2–6].

Two models have been proposed for the mechanism of dehydration of  $\text{Mg}(\text{OH})_2$ . Thus, Goodman [7] assumes that water is lost, in a similar manner, from all the regions of the crystallites. Hydroxyl groups from adjacent layers combine to form water that can diffuse away. In contrast, Ball and Taylor [8] and Brindley [9] assumed that the reaction takes place simultaneously throughout the crystal bulk, developing “donor” and “acceptor” regions during the decomposition process;  $\text{Mg}^{2+}$  ions migrate from the former to the latter with a counter-migration of protons. The acceptor regions thus become  $\text{MgO}$  crystallites, whilst protons combine with hydroxyl ions to form water molecules which escape from the donor regions. The

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\* Author to whom correspondence should be addressed.

work of Niepce et al. [4] supports the model of Goodman, but some uncertainty remains.

With regard to  $\beta$ -Cd(OH)<sub>2</sub>, kinetic studies performed by TGA [10] and time resolved X-ray diffraction (TRXD) [11] showed the water loss and the formation of cadmium oxide not to be concomitant temporally, kinetically or mechanistically. A number of effects (surface energy effects due to adsorbed water, thermal disruption of the lattice and the role of unspecified defects) are tentatively suggested to be responsible for the inconsistent results for decomposition kinetics.

In both cases CDRTA appears to be a technique capable of elucidating the decomposition mechanism of these hydroxides.

## EXPERIMENTAL

Thermal runs were performed in equipment made in our laboratory according to the specifications kindly given by Rouquerol [12] and described in ref. 13. The total decomposition pressure was in the range from  $10^{-2}$  to  $4 \times 10^{-2}$  mmHg.

Magnesium hydroxide was supplied by Merck (Germany), and cadmium hydroxide was obtained by hydrolysis of cadmium acetate [14] and identified by X-ray powder diffraction as the  $\beta$ -phase.

## RESULTS AND DISCUSSION

Characteristic curves representing the decomposition processes of Mg(OH)<sub>2</sub> and  $\beta$ -Cd(OH)<sub>2</sub> are shown in Figs. 1 and 2, respectively. In these curves we can distinguish three zones.

(1) Firstly temperature and pressure increase, and, when the pre-set pressure value is reached, temperature regulation of the furnace begins.

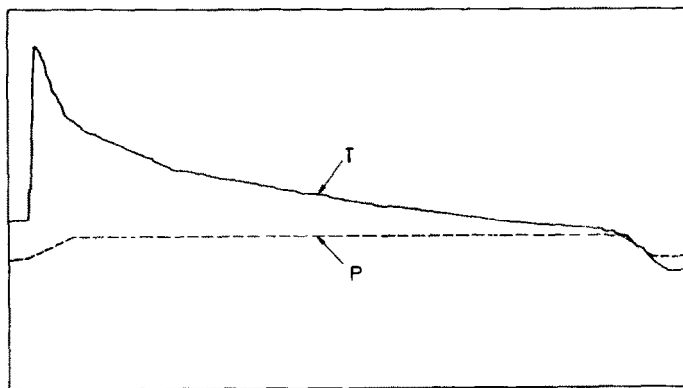


Fig. 1. Experimental CDRTA curves for the dehydration of magnesium hydroxide (brucite): *T*, temperature; *P*, pressure.

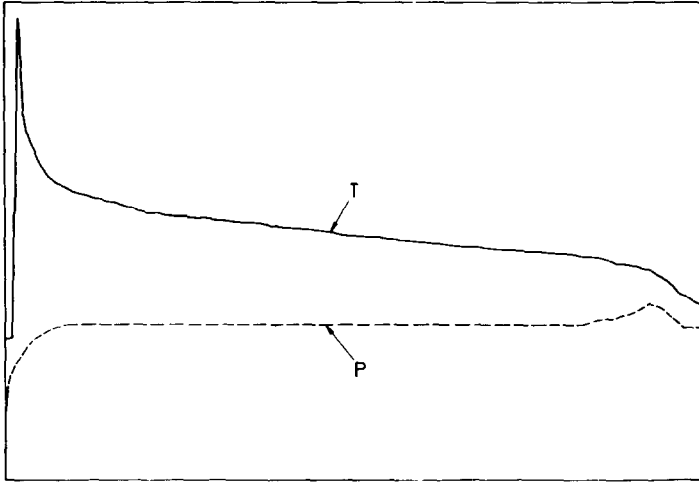


Fig. 2. Experimental CDRTA curves for the dehydration of  $\beta$ -cadmium hydroxide:  $T$ , temperature;  $P$ , pressure.

- (2) Pressure is maintained constant and the temperature increase is slow.
- (3) Finally, a sudden temperature increase and pressure drop show the end of the decomposition reaction, and the thermal run finishes.

Kinetic analysis was performed, by using the seven kinetic equations [15] shown in Table 1, in the following way. Assuming the general equation

$$\frac{d\alpha}{dt} = A \exp(-E^*/RT) f(\alpha)$$

and given that

$$\frac{d\alpha}{dt} = C \text{ (constant)}$$

TABLE 1

Equations used for the kinetic analysis

No.	$f(\alpha)$	Mechanism	
1	$1/2$	D1	Unidimensional diffusion
2	$[-\ln(1-\alpha)]^{-1}$	D2	Bidimensional diffusion
3	$1.5(1-\alpha)^{2/3}$	D3	Tridimensional diffusion (Jander equation)
4	$\frac{1-(1-\alpha)^{1/3}}{[1.5(1-\alpha)^{-1/3}]^{-1}}$	D4	Tridimensional diffusion (Ginstling-Brounstein equation)
5	$(1-\alpha)$	F1	Random nucleation
6	$2(1-\alpha)^{1/2}$	R2	Contracting cylinder
7	$3(1-\alpha)^{2/3}$	R3	Contracting sphere

TABLE 2

Data corresponding to the decomposition of  $\text{Mg}(\text{OH})_2$ . Reaction rate = C

$\alpha$	$T$ (K)	$\alpha$	$T$ (K)
0.20	427.6	0.55	434.8
0.25	428.5	0.60	436.1
0.30	429.4	0.65	437.4
0.35	430.4	0.70	439.2
0.40	431.4	0.75	441.6
0.45	432.5	0.80	448.8
0.50	433.6		

TABLE 3

Data corresponding to the decomposition of  $\text{Mg}(\text{OH})_2$ . Reaction rate =  $C/5.561$ 

$\alpha$	$T$ (K)	$\alpha$	$T$ (K)
0.20	426.5	0.55	432.9
0.25	427.2	0.60	433.8
0.30	427.9	0.65	434.8
0.35	428.6	0.70	436.0
0.40	429.4	0.75	438.0
0.45	431.2	0.80	441.2
0.50	432.0		

in the experimental conditions imposed by the technique, we can write

$$\frac{C}{A} = \exp(-E^*/RT) f(\alpha) \quad (1)$$

and therefore

$$\ln\left(\frac{C}{A}\right) = -\frac{E^*}{RT} + \ln f(\alpha) \quad (2)$$

TABLE 4

Data corresponding to the decomposition of  $\text{Mg}(\text{OH})_2$ . Reaction rate =  $C/9.233$ 

$\alpha$	$T$ (K)	$\alpha$	$T$ (K)
0.20	425.1	0.55	429.5
0.25	425.6	0.60	430.3
0.30	426.1	0.65	431.2
0.35	426.6	0.70	432.1
0.40	427.3	0.75	434.1
0.45	428.0	0.80	436.8
0.50	428.7		

TABLE 5

Results obtained from the representation of eqn. (3) for the decomposition of  $\text{Mg}(\text{OH})_2$ 

Mechanism	Rate		C						
	C		C/5.561			C/9.233			
	$r^a$	$s$	$r$	$i$	$s$	$r$	$i$	$s$	
D1	0.996	-36.23	20111.0	0.999	-35.68	19886.0	0.995	-35.02	19626.0
D2	0.997	-40.33	25196.0	0.999	-41.99	25213.0	0.998	-42.51	25327.0
D3	0.993	-100.23	34342.0	0.998	-106.74	35902.0	0.998	-112.20	36000.0
D4	0.993	-29.17	34300.0	0.998	-30.87	35926.0	0.998	-34.12	35929.0
F1	0.981	-18.77	14211.0	0.991	-20.21	15086.0	0.986	-19.30	15134.0
R2	0.981	-25.34	7034.0	0.991	-27.39	6819.0	0.986	-28.15	6513.0
R3	0.982	-29.29	9926.0	0.991	-32.22	10031.0	0.986	-33.62	10877.0

<sup>a</sup>  $r$  is the correlation coefficient,  $i$  is the intercept value,  $s$  is the slope.

or

$$\ln f(\alpha) = \frac{E^*}{RT} + \ln\left(\frac{C}{A}\right) \quad (3)$$

Thus, a plot of  $\ln f(\alpha)$  versus  $1/T$  will be a straight line of slope  $E^*/R$  for the  $f(\alpha)$  function that best fits the kinetics of the process.

Tables 2, 3 and 4 give the results obtained for the decomposition reaction of  $\text{Mg}(\text{OH})_2$  at three different decomposition rates of relative values  $C$ ,  $C/5.561$  and  $C/9.233$ .

Table 5 shows the results obtained from eqn. (3) for these processes, using the seven kinetic equations collected in Table 1. We can see that correlation coefficients are near to 1 and, therefore, we cannot distinguish the mechanisms on the basis of these representations.

Nevertheless, we can use these results in another way: taking into account eqn. (1), we can write for two decomposition rates  $C_1$  and  $C_2$  and the same value of the decomposition degree

$$\frac{C_1}{A} = \exp(-E^*/RT_1)f(\alpha)$$

$$\frac{C_2}{A} = \exp(-E^*/RT_2)f(\alpha)$$

and, in consequence

$$\ln \frac{C_1}{C_2} = \frac{E^*}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

TABLE 6

Values of  $E^*/R$  calculated from the observed temperature differences at various values of  $\alpha = \text{constant}$  for the decomposition of  $\text{Mg}(\text{OH})_2$

$\alpha$	Relationship of rates		
	1/5.561	5.561/9.233	1/9.233
0.20	25198.3	25201.8	25238.8
0.25	25199.1	25200.6	25229.1
0.30	25199.1	25198.8	25230.2
0.35	25186.8	25208.6	25233.1
0.40	25200.0	25209.9	25216.8
0.45	25133.4	25205.7	25230.3
0.50	25212.0	25210.1	25235.9
0.55	25220.3	25212.3	25238.2
0.60	25218.6	25226.1	25244.0
0.65	25226.2	25224.7	25238.9
0.70	25225.9	25228.8	25242.2
0.75	25236.3	25231.3	25250.1
0.80	25235.4	25232.0	25256.4
Mean value	25200.9	25214.5	25237.2

TABLE 7

Data corresponding to the decomposition of  $\beta$ -Cd(OH)<sub>2</sub>. Reaction rate =  $C$ 

$\alpha$	$T$ (K)	$\alpha$	$T$ (K)
0.20	341.6	0.55	348.4
0.25	342.3	0.60	349.8
0.30	343.1	0.65	351.5
0.35	344.0	0.70	353.4
0.40	345.0	0.75	355.7
0.45	346.0	0.80	358.5
0.50	347.1		

TABLE 8

Data corresponding to the decomposition of  $\beta$ -Cd(OH)<sub>2</sub>. Reaction rate =  $C/4.926$ 

$\alpha$	$T$ (K)	$\alpha$	$T$ (K)
0.20	324.0	0.55	330.1
0.25	324.6	0.60	331.3
0.30	325.3	0.65	332.8
0.35	326.1	0.70	334.5
0.40	327.0	0.75	336.6
0.45	327.9	0.80	339.1
0.50	328.9		

TABLE 9

Data corresponding to the decomposition of  $\beta$ -Cd(OH)<sub>2</sub>. Reaction rate =  $C/9.920$ 

$\alpha$	$T$ (K)	$\alpha$	$T$ (K)
0.20	316.8	0.55	322.6
0.25	317.4	0.60	323.8
0.30	318.1	0.65	325.3
0.35	318.8	0.70	326.9
0.40	319.7	0.75	328.9
0.45	320.6	0.80	333.1
0.50	321.4		

Equation (4) shows that we can obtain the activation energy value from the temperatures  $T_1$  and  $T_2$  corresponding to the same reaction degree at two reaction rates  $C_1$  and  $C_2$ .

In Table 6 the results of this analysis are given: we can see that a value of ca. 25 200 K is obtained for  $E^*/R$ , and thus a D2 mechanism in Table 5 is unambiguously selected. In this way, an easy determination of the mechanism and kinetic parameters is performed by a combination of both analysis methods.

A similar study was made for the decomposition reaction of  $\beta$ -Cd(OH)<sub>2</sub>. In Tables 7–9, decomposition data for the relative rates  $C$ ,  $C/4.926$  and  $C/9.920$  are reported. Analysis according to eqn. (3) is shown in Table 10, in

TABLE 10  
Results obtained from the representation of eqn. (3) for the decomposition of  $\beta$ -Cd(OH)<sub>2</sub>

Mechanism	Rate		C/4.926						C/9.920						
	C		r		i		s		r		i		s		
	r <sup>a</sup>	s	r	s	r	s	r	s	r	s	r	s	r	s	
D1	0.934	-26.78	0.933	9351.7	-28.33	9369.7	0.931	-28.80	9310.8	0.964	-38.76	13667.3	0.963	-41.72	13585.0
D2	0.964	-38.76	0.964	13638.1	-41.02	13667.3	0.970	-45.77	15332.6	0.971	-42.42	15389.7	0.970	-45.77	15332.6
D3	0.972	-42.42	0.971	15389.7	-44.98	15423.7	0.979	-56.36	18663.1	0.981	-52.27	18729.2	0.979	-56.36	18663.1
D4	0.981	-52.27	0.980	18729.2	-55.39	18772.7	0.998	-15.19	9991.9	0.999	-29.56	10019.0	0.998	-15.19	9991.9
F1	0.999	-29.56	0.999	10019.0	-14.92	10046.0	0.998	-15.19	4996.1	0.999	-14.08	5009.5	0.998	-15.19	4996.1
R2	0.999	-14.08	0.999	5009.5	-19.72	6697.2	0.998	-20.08	6661.6	0.999	-18.60	6679.3	0.998	-20.08	6661.6
R3	0.999	-18.60	0.999	6679.3											

<sup>a</sup>  $r$  is the correlation coefficient,  $i$  is the intercept value,  $s$  is the slope.



TABLE 11

Values of  $E^*/R$  calculated from the temperature differences at various values of  $\alpha = \text{constant}$  for the decomposition of  $\beta\text{-Cd}(\text{OH})_2$

$\alpha$	Relationship of rates		
	1/4.926	4.926/9.920	1/9.920
0.20	10027.3	9979.5	10012.7
0.25	10009.6	10017.0	10011.8
0.30	9998.1	10060.8	10017.1
0.35	9992.8	9969.2	9985.6
0.40	9993.7	10025.0	10003.2
0.45	9994.7	10080.8	10020.8
0.50	10001.8	9866.5	9960.1
0.55	10020.9	9939.4	9995.9
0.60	9988.5	10012.7	9995.9
0.65	9974.7	10104.6	10014.0
0.70	9973.2	10071.9	10003.1
0.75	9995.3	10064.7	10016.4
0.80	9991.9	10082.5	10019.4
Mean value	9997.1	10021.1	10004.3

which we again found correlation coefficients that are not capable of distinguishing the mechanism of the decomposition process. Nevertheless (see Table 11), the value obtained (ca. 10000 K) for  $E^*/R$  indicates in Table 10 an F1 mechanism (although in this case D1 kinetics could be also possible).

We can conclude that CDRTA permits the easy and unambiguous collection and analysis of kinetic data for thermal decomposition processes.

#### ACKNOWLEDGEMENTS

The authors thank Dr. J. Rouquerol for the facilities provided concerning the design and installation of the CDRTA technique. This work was financially supported by the Spanish CICYT.

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