Thermochimica Acta, 38 (1980) 117—123

STUDY OF THE THERMAL DECOMPOSITION REACTION MECHANISM OF ALKALINE-EARTH CARBONATES UNDER HIGH VACUUM BY BOTH THERMOGRAVIMETRIC ANALYSIS AND CONSTANT DECOMPOSITION RATE THERMAL ANALYSIS TECHNIQUES

J.M. CRIADO *, F. ROUQUEROL and J. ROUQUEROL

Centre de Recherches de Microcalorimétrie et de Thermochimie du C.N.R.S., 26, rue du 141ème R.I.A., 13003 Marseille (France)

(Received 15 November 1979)

ABSTRACT

Both thermogravimetric analysis (TG) and constant rate thermal analysis (CRTA) under high vacuum were applied to the study of the mechanism of thermal decomposition of alkaline-earth carbonates. Proper experimental conditions were used in order to avoid heat and mass transfer phenomena. The kinetic analysis of TG and CRTA curves was carried out taking into account the kinetic laws of the mechanisms of solid state reactions most commonly used in the literature. Good agreement between the activation energy and the Arrhenius pre-exponential factor calculated from both techniques is only obtained when considering that the decomposition of alkaline-earth carbonates follows first-order kinetics.

A compensation effect was found for the above reactions between the logarithm of the Arrhenius pre-exponential factor and the activation energy. This behaviour was interpreted by a correlation between the stability of the salts and the mobility of the CO_3^{2-} ion present in the activated complex.

INTRODUCTION

It has been shown in previous papers [1,2] that the kinetic analysis of a single TG trace does not allow the discrimination between Avrami—Erofeev, "n order" and diffusion controlled reactions although, on the other hand, it is theoretically possible [3] to distinguish them using the constant decomposition rate thermal analysis technique (CRTA) [4]. However, the latter procedure (use of one CRTA curve) has the limitation that solid state reactions following n_1-order kinetics ($n \neq 0$) with an activation energy E_1 necessarily fit any kinetic law of n order giving an activation energy $E = (n/n_1)\,E_1$. This means that one "standard" CRTA curve does not supply enough information for calculating n when it is different from 0. There are two possible ways of providing the missing information: either to carry out a special CRTA experiment, with alternative control at two different rates of decom-

---

* Permanent address: Departamento de Quimica Inorgânica, Facultad de Ciencias, Universidad de Sevilla, Seville, Spain.

position (this single experiment leading unambiguously to the energy of activation without the need of assuming any order of reaction [4]), or to carry out an extra TG experiment. It seems, from a former work [3], that the simultaneous kinetic analysis of thermogravimetric diagrams obtained under a linear heating program and a constant rate of thermal decomposition, respectively, provides an excellent procedure for discerning the proper mechanism of solid state reactions.

The scope of the present work, therefore, is to apply both TG and CRTA techniques to the study of the mechanism of thermal decomposition of alkaline-earth carbonates.

EXPERIMENTAL

Calcium, strontium and barium carbonates from d'Hermio (A.R. grade) and magnesite from Navarra (Spain) were used. The composition of the magnesite was: MgO 45.35%; SiO_2 1.76%; Fe_2O_3 1.12%; Al_2O_3 0.32%; CaO 0.98%; loss on ignition 50.50%.

A Mettler thermoanalyzer with a platinum crucible of 16 mm diameter was employed. The apparatus has been modified in order to monitor the furnace temperature in such a way that the total decomposition rate remains constant over the decomposition range. This has been attained both by controlling the residual pressure in the close vicinity of the sample and by maintaining a constant value of the pumping rate which can be selected by means of a butterfly valve.

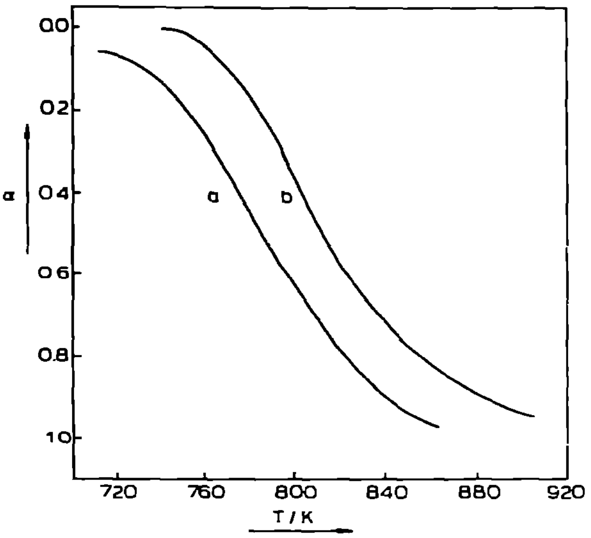
It is worth pointing out that the thermoanalyzer was modified without losing its original performance from the suppliers. Therefore, it is also possible to record TG diagrams at linear heating rate ranging from 0.5 K min^{-1} to 25 K min^{-1}.

The CRTA diagrams of alkaline-earth carbonates were recorded using a constant CO_2 residual pressure of 4×10^{-5} torr and a constant specific decomposition rate of about 5×10^{-3} mg of vapour lost per min and per mg of starting sample, i.e. of about 5×10^{-3} min^{-1}. The sample sizes ranged from 20 to 32 mg. Under these experimental conditions mass and heat transfer effects seem to be avoided, as shown elsewhere [5].

In order to obtain the TG diagrams the samples were previously outgassed at room temperature down to the best vacuum available (2×10^{-6} torr). A heating rate of 0.5 K min^{-1} and sample sizes as small as 1—3 mg were used in order to avoid heat and mass transfer problems. In this way, the pressure recorded throughout the experiment did not exceed 2×10^{-6} torr.

RESULTS AND DISCUSSION

Figures 1—4 show the TG and CRTA curves obtained for $MgCO_3$, $CaCO_3$, $SrCO_3$, and $BaCO_3$, respectively. In order to perform the kinetic analysis of these diagrams, it is necessary to take into account that the general expression of the reaction rate of the thermal decomposition of a solid is



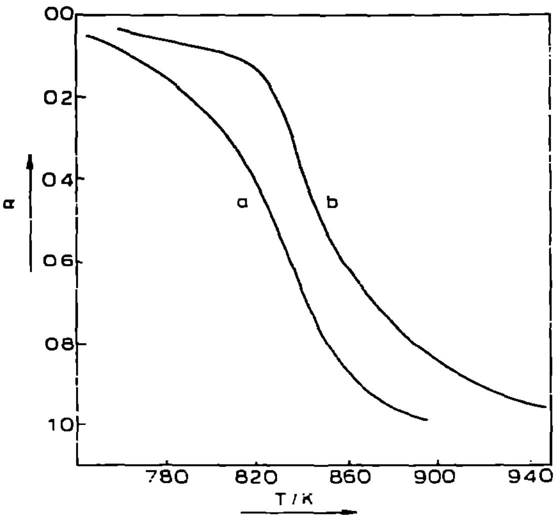


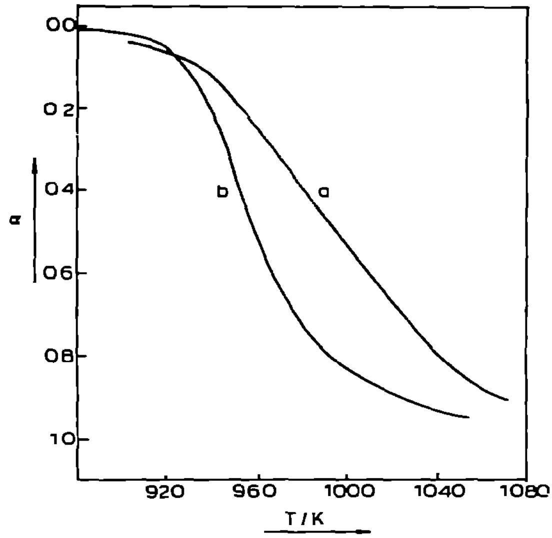
Fig. 1. Thermoanalytical curves for $MgCO_3$. a, TG; b, CRTA.

Fig. 2. Thermoanalytical curves for $CaCO_3$. a, TG; b, CRTA.

$$\frac{d\alpha}{dt} = A\, e^{-E/RT} f(\alpha) \qquad (1)$$

where α is the molar extent of reaction referred to 1 mole of starting material, $f(\alpha)$ is a function depending on the reaction mechanism, and the other letters have their usual meaning.

If we bear in mind that CRTA diagrams are obtained at a constant decomposition rate, $C = d\alpha/dt$, eqn. (1) becomes



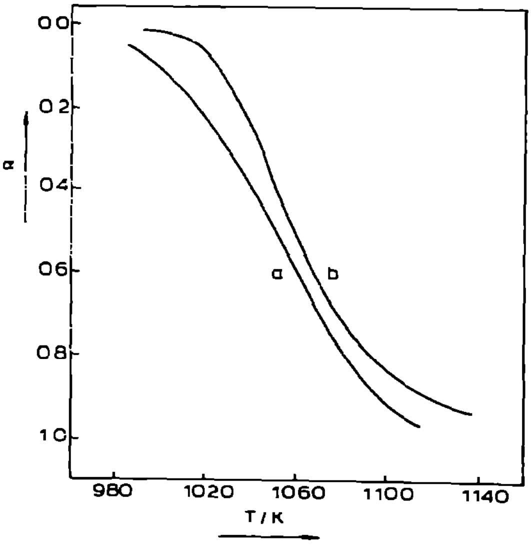


Fig. 3. Thermoanalytical curves for $SrCO_3$. a, TG; b, CRTA.

Fig. 4. Thermoanalytical curves for $BaCO_3$. a, TG; b, CRTA.

$$\ln \frac{1}{f(\alpha)} = \ln \frac{A}{C} - \frac{E}{RT} \qquad (2)$$

Therefore, the kinetic parameters of the reaction can be obtained from the plot of the left-hand side of eqn. (2) against the reciprocal of the temperature.

Analysis of the TG diagrams has been carried out by the method of Coats and Redfern [6].

$$\ln g(\alpha) - 2 \ln T = \ln \frac{AR}{E\beta} - \frac{E}{RT} \qquad (3)$$

where β is the heating rate, and $g(\alpha)$ is a function depending on the reaction mechanism and connected with the function $f(\alpha)$ through the expression

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha \qquad (4)$$

The plot of the left-hand side of eqn. (3), after selecting the proper function $g(\alpha)$, vs. the reciprocal of the temperature should be a straight line from whose slope and intercept the kinetic parameters would be obtained.

The kinetic analysis of the CRTA and TG curves included in Figs. 1—4 has been performed by means of eqns. (1) and (3), respectively, after introducing the $f(\alpha)$ and $g(\alpha)$ functions of the mechanisms of solid state reactions more usually employed in the literature. As an example, the results obtained from the kinetic analysis of the thermal decomposition of $CaCO_3$ are included in Table 1. We can see that good agreement between the kinetic parameters calculated from TG and CRTA diagrams is only obtained if we assume that the reaction follows either first-order kinetics (F_1) or an Avrami—Erofeev mechanism with $m = 2$ (A_2). However, a very poor regression coefficient is obtained from the kinetic analysis of the CRTA curve assuming that the reaction obeys the A_2 mechanism. This means that the experimental data fit the F_1 mechanism much better, as Fig. 5 clearly shows. Accordingly, we conclude that the thermal decomposition of $CaCO_3$ is here following first-order kinetics.

Similar results were obtained from the kinetic analysis of all the alkaline-earth carbonates, as shown in Table 2 which collects the activation energies and Arrhenius pre-exponential factors calculated from both TG and CRTA curves assuming an F_1 mechanism.

The data of Tables 1 and 2 show that the analysis of both a TG and a CRTA curve supply an interesting procedure for determining, simply by means of kinetic methods, the actual mechanism of the thermal decomposition of solids, as suggested in a previous paper [3].

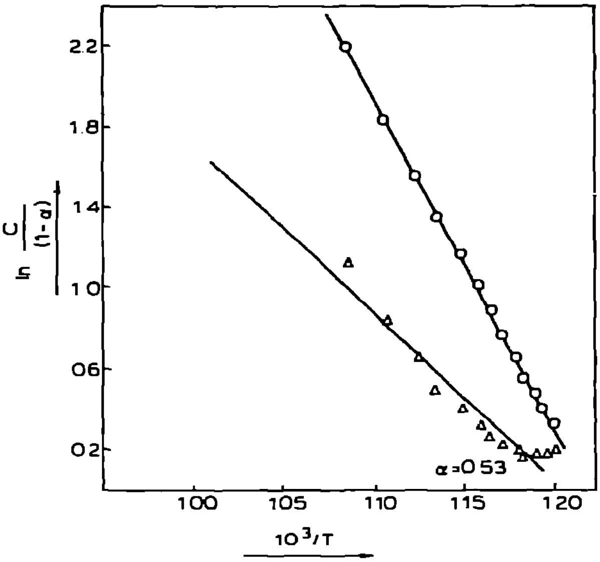
Figure 6 indicates that a compensation effect exists between the activation energy and the Arrhenius pre-exponential factor of the thermal decomposition of alkaline-earth carbonates. This fact may be explained assuming that the reaction takes place through an activated complex of similar structure. Thus, the higher the stability of the carbonate, the lower the mobility of CO_3^{2-} ion involved in the activated complex, so increasing the activation entropy, ΔS^*, and, therefore, $\ln A$ in agreement with the absolute reaction rate theory. This interpretation [7] may be supported by the fact that both

TABLE 1

Kinetic parameters of the thermal decomposition of $CaCO_3$ calculated from TG and CRTA curves by assuming various reaction mechanisms

Mechanism *	TG (β = 0.5°C min^{-1})			CRTA ($C = 5 \times 10^{-3}$ min^{-1})		
	E (kcal $mole^{-1}$)	A (min^{-1})	Regression coefficient	E (kcal $mole^{-1}$)	A (min^{-1})	Regression coefficient
R_2	32.4	2.8×10^{6}	−0.9965	16.7	3.0×10^{4}	−0.9995
R_3	35.0	1.3×10^{7}	−0.9972	22.3	4.5×10^{3}	−0.9995
F_1	35.0	8.0×10^{6}	−0.9974	34.0	5.0×10^{6}	−0.9995
A_2	36.5	2.0×10^{2}	−0.9963	34.0	4.5×10^{3}	−0.9652
A_3	33.2	9.1×10^{-4}	−0.9956	33.5	1.0×10^{0}	−0.8800
D_1	56.0	3.6×10^{37}	−0.9918	40.0	2.0×10^{7}	−0.9213
D_2	63.4	2.1×10^{14}	−0.9954	3.5	3.4×10^{-2}	−0.6450
D_3	73.0	2.2×10^{16}	−0.9975	52.5	3.7×10^{10}	−0.8776
D_4	66.0	3.6×10^{14}	−0.9964	39.4	1.2×10^{7}	−0.9745

* The symbols of Sharp et al. [9] have been used.



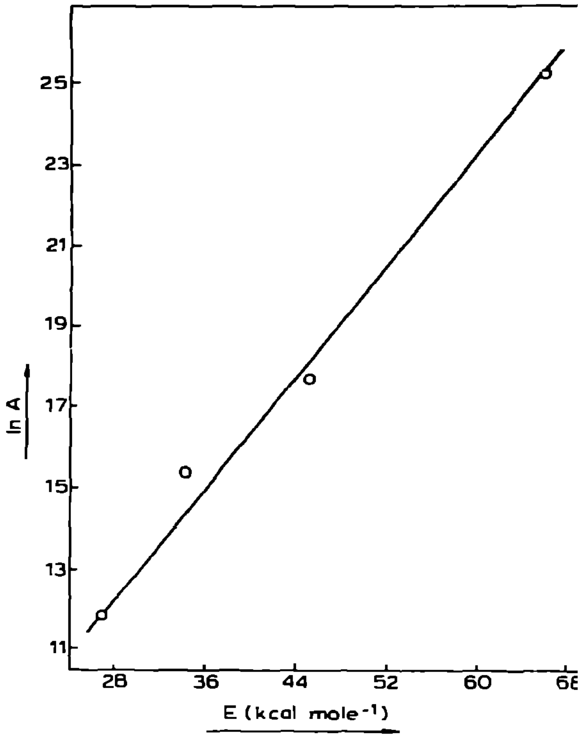


Fig. 5. Kinetic analysis of CRTA curve of Fig. 2. (○) F_1 mechanism (slope proportional to E/R; (△) A_2 mechanism (slope proportional to $E/2R$).

Fig. 6. Compansation effect between the activation energy and the logarithm of the Arrhenius pre-exponantial factor of the alkaline-earth carbonates.

the activation energies of thermolysis and the standard enthalpies of formation from CO_2 and from the oxide roughly follow a similar trend.

It is necessary to point that the thermal decomposition of alkaline-earth carbonates was also studied previously [8] under vacuum using the same samples as used here. The activation energies varied in the same way, although the values reported here are, in general, somewhat lower than those

TABLE 2

Kinetic analysis of TG and CRTA curves of alkaline-earth carbonates assuming a first-order law

Sample	TG (β = 0.5°C min^{-1})		CRTA (C = 5 × 10^{-3} min^{-1})	
	E (kcal mole^{-1})	A (min^{-1})	E (kcal mole^{-1})	A (min^{-1})
$MgCO_3$	28.2	5.3 × 10^{5}	27.0	1.4 × 10^{5}
$CaCO_3$	35.0	8.0 × 10^{6}	34.0	5.0 × 10^{6}
$SrCO_3$	42.3	1.3 × 10^{7}	45.1	4.8 × 10^{7}
$BaCO_3$	65.2	3.7 × 10^{11}	65.9	1.0 × 10^{11}

given in ref. 8. On the other hand, a "sphere-contracting" Hume—Colvin mechanism was reported [8] for the thermal decomposition of the salts. This disagreement may perhaps find an explanation in the fact that these previous experiments were carried out (i) with larger samples (20—40 mg), (ii) with higher heating rates (5—12 K min^{-1}), and (iii) without the efficient pressure control of the environment which we were able to achieve in the present work. We have proved in other works [5] that even under a dynamic vacuum it is very important to monitor the actual pressure in the close vicinity of the sample in order to obtain reliable kinetic data.

ACKNOWLEDGEMENTS

One of us (J.M.C.) thanks the French C.N.R.S. and the Spanish C.S.I.C. for a grant and a leave of absence, respectively.

REFERENCES

1 J.M. Criado and J. Morales, Thermochim. Acta, 16 (1976) 382.
2 J.M. Criado and J. Morales, Thermochim. Acta, 19 (1977) 305.
3 J.M. Criado, Thermochim. Acta, 28 (1979) 307.
4 J. Rouquerol, Proc. 2nd Int. Conf. Therm. Anal., Vol. I, Worcester, U.S.A., 1968, Academic Press, New York, 1969, p. 281; J. Therm. Anal., 5 (1973) 203.
5 J.M. Criado, F. Rouquerol and J. Rouquerol, Thermochim. Acta, 38 (1980) 109.
6 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
7 E. Cremer, Adv. Catal., 7 (1955) 75.
8 J.M. Criado, F. Gonzalez and J. Morales, Proc. First Europ. Symp. Therm. Anal., Heyden, London, 1976, p. 258.
9 J.H. Sharp, G.W. Brindley and N.N. Achar, J. Am. Ceram. Soc., 47 (1966) 379.