Thermochimica Acta, 152 (1989) 329–334
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

KINETIC STUDY BY MASS SPECTROMETRY AND CALCULATION OF THE ENTHALPY OF DECOMPOSITION OF BASIC NICKEL CARBONATE

M.M. ROMERO

I.S.M.M., Moa, Holguín (Cuba)

J.C. LLÓPIZ

I.M.R.E., Facultad de Química, Universidad de la Habana, La Habana (Cuba)

A. JEREZ, C. PICO and M.L. VEIGA *

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

(Received 25 January 1989)

ABSTRACT

The thermal decomposition of basic nickel carbonate was studied by mass spectrometry. The kinetic parameters for the processes leading to the production of H_2O and CO_2 were determined and the total enthalpy for the evolution of CO_2 was calculated.

INTRODUCTION

Mass spectrometry has been used by several workers [1–5] to study the kinetics of solid state decomposition reactions. Since a mass spectrometer can both identify and quantify the gaseous products, the technique contributes to the understanding of the decomposition mechanism as well as to the determination of the kinetic parameters. The method is based [4] on the fact that the ion current I measured for a characteristic mass spectral ion is proportional to the rate of gas evolution from the decomposing solid and to the rate of weight loss during non-isothermal heating.

The decomposed fraction of the sample correlates with the ion current for a given time or temperature x as follows

$$\alpha_x = \frac{\sum_0^{\infty} I_x - \sum_x^{\infty} I_x}{\sum_0^{\infty} I_x} \qquad (1)$$

showing the course of the reaction.

---

* Author to whom correspondence should be addressed.

The partial pressure P_i of the ith component in the Knudsen cell can be determined [6] by

$$P_i = K_i I_i T \qquad (2)$$

where K_i is constant for a constant m/e ratio and I_i is the ion current for the ith component.

The decomposition enthalpy ΔH_r is a function of the partial pressure of the evolved gas according to

$$\frac{\Delta H_r}{RT^2} = \frac{\mathrm{d}\ln P}{\mathrm{d}T} \qquad (3)$$

where R is the gas constant.

From eqns. (2) and (3) it is evident [7] that

$$-\frac{\Delta H_x}{R} = \frac{\mathrm{d}(\ln I_i T)}{\mathrm{d}(1/T)} \qquad (4)$$

Thus the values of ΔH_x can be obtained through the evaluation of the slope in an $R\ \ln(I_i T)$ vs. $1/T$ plot.

The total reaction enthalpy ΔH can be calculated by taking into account [8] that

$$E = \Delta H - \Delta H_x$$

in which the activation energy E and ΔH_x have to be previously evaluated.

In this work a kinetic study of the thermal decomposition in vacuo of anhydrous basic nickel carbonate (pure reagent) and the calculation of the total enthalpy H for the CO_2 evolved are reported. In order to establish the most probable mechanism in each transformation, the method of kinetic analysis of Jerez et al. [9] was employed, using 24 functions $f(\alpha)$ which describe different kinetic models. Some of these functions are summarized in ref. 10 and analysed in ref. 11.

EXPERIMENTAL

Measurements were carried out in a Leybold QUADRUVAC-200 quadrupole mass spectrometer attached to a vacuum system with a sample container heated by a Chesa furnace controlled by a Rockwell AIM-65 microcomputer. The heating rate was 3.5 K min^{-1} and the ion current was monitored for constant m/e ratios, firstly 18 (H_2O^+ ions) and later 44 (CO_2^+ ions). α values were calculated from the ion current curves.

Anhydrous basic nickel carbonate of nominal composition $NiCO_3$ $2Ni(OH)_2$was supplied by Carlo Erba (pure reagent).

Thermal decomposition reactions of this material were also studied by conventional thermogravimetry in a Mettler TA3000 thermoanalyser.

RESULTS AND DISCUSSION

From the mass spectrum scanned for $m/e = 18$ and $m/e = 44$ the temperatures of maximum evolution of water and carbon dioxide were localized at 405 K and 465 K respectively; this indicates that although the evolution of H_2O and CO_2 takes place simultaneously in the temperature range 342–517 K, it is not a single process; there are actually two different reactions. Figure 1 shows the I vs. T plot for both mass spectrum ions. The corresponding $m/e = 18$ curve shows two peaks with maxima at 308 and 405 K. The first peak, due to its low temperature, can be attributed to loss of adsorbed water. Therefore the kinetic study was performed from the second peak which corresponds to the process

$$NiCO_3 \cdot 2Ni(OH)_2 \rightarrow NiCO_3 \cdot 2NiO + 2H_2O$$

with $\alpha_{max} = 0.505$ at 405 K. In Fig. 2(a) the corresponding α vs. T plot is represented, showing a characteristic sigmoid form with a relatively long induction period. Calculations allow us to conclude that this process occurs by diffusion with decreasing reactant activity, according to a D5 [12] kinetic model described by the following functions

$$f(\alpha) = (1-\alpha)^{4/3}\left[(1-\alpha)^{-1/3} - 1\right]$$

$$g(\alpha) = \tfrac{3}{2}\left[(1-\alpha)^{-1/3} - 1\right]$$

The activation energy $E = 105$ kJ mol^{-1} and the pre-exponential Arrhenius factor $A = 2.2 \times 10^{10}$ s^{-1} were obtained with a correlation coefficient of 0.9995.

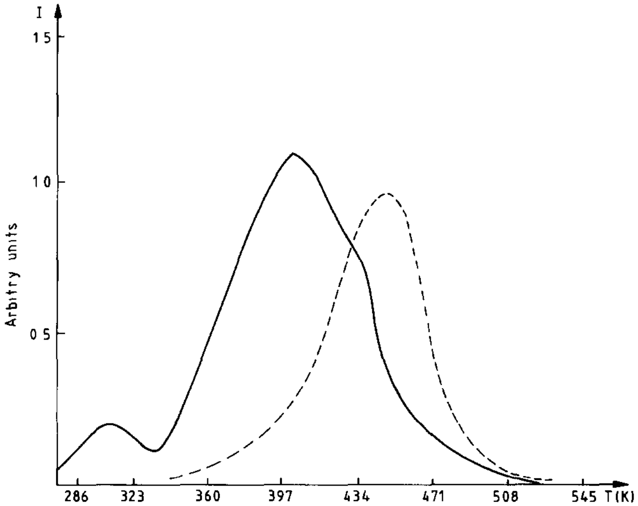

Fig. 1. Ion current curves for H_2O^+ (———) and CO_2^+ (— — —).

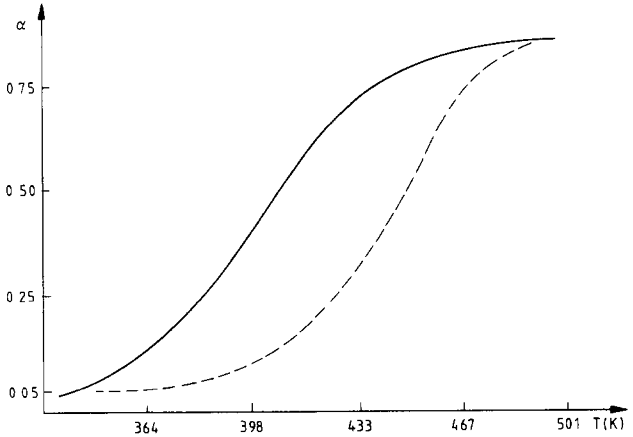

Fig. 2. α vs. T curves obtained from I vs. T curves: $m/e = 18$ (———); $m/e = 44$ (— — —).

For the evolution of CO_2

$NiCO_3 \cdot 2NiO \rightarrow 3NiO + CO_2$

the I vs. T curve (Fig. 1(b)) shows a long acceleration period until a maximum is reached at 449 K ($\alpha_{max} = 0.623$). Figure 2(b) shows the corresponding α vs. T curve. Kinetic results are given in Tables 1 and 2. Table 1 shows the results obtained by dividing the α vs. T curve into three sections, two for the induction step and the third corresponding to the decrease in the ion current curve. The kinetic parameter values decrease notably in the last section. In Table 2 the results of the analysis of the CO_2 evolution process are presented for four different temperature ranges.

TABLE 1

Kinetic results of the evolution of CO_2 for three ranges of degree of transformation

$\Delta\alpha$ interval	Mechanism	E (kJ mol^{-1})	A (s^{-1})	r
0.001–0.094	D5	162.8	2.11×10^{16}	0.9951
0.132–0.627	D5	162.0	9.75×10^{15}	0.9995
0.735–0.997	D5	147.6	2.76×10^{14}	0.9669

TABLE 2

Kinetic results of the evolution of CO_2 for different temperature ranges

ΔT (K)	Mechanism	E (kJ mol^{-1})	A (s^{-1})	r
351–449	D5	157.01	2.51×10^{15}	0.9985
351–475	D5	159.49	5.48×10^{15}	0.9989
351–513	D5	158.25	3.74×10^{15}	0.9984
409–513	D5	160.46	6.50×10^{15}	0.9946

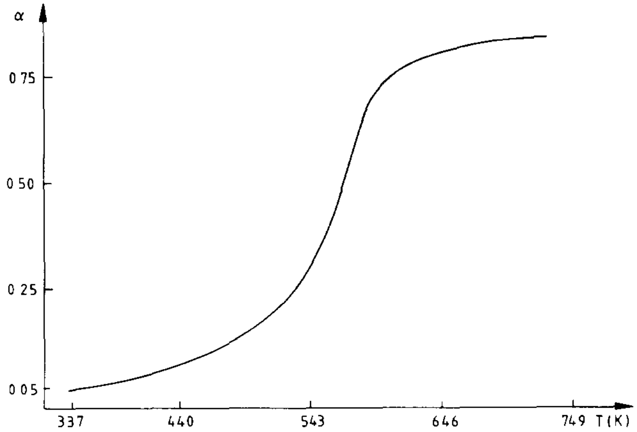

Fig. 3. α vs. T curve obtained from thermogravimetry of basic nickel carbonate.

The linearity between ln A and E was obtained with correlation coefficients of 0.9994 and 0.9975 from the results shown in Tables 1 and 2. Therefore, it can be concluded that the compensation effect [13] is valid in the kinetic parameters.

Figure 3 shows the α vs. T curve obtained from the single step of weight loss observed by conventional thermogravimetry, which suggests a unique decomposition process. Nevertheless mass spectrometry reveals that this is not so. Kinetic analysis of this curve indicates a D5 kinetic model with $E = 88.5$ kJ mol^{-1} and $A = 5.3 \times 10^4$ s^{-1}; these results are very different from those calculated for the separate elementary reactions. This is expected as the processes overlap during the decomposition and cannot be distinguished by thermogravimetry.

Using the procedure described above, a value of $\Delta H_x = 62.5$ kJ mol^{-1} was calculated for the evolution of CO_2 with a correlation coefficient of 0.994; this leads to an enthalpy value of $\Delta H = 221.3$ kJ mol^{-1} for this process in the thermal decomposition of anhydrous basic nickel carbonate.

ACKNOWLEDGEMENT

We wish to acknowledge Lic. Andrés Novoa Castiel for his help with the computer programs.

REFERENCES

1 D. Dollimore, J.P. Gupta, N.J. Manning and D.V. Nowell, Thermochim. Acta, 31 (1979) 357.
2 D. Price, D. Dollimore, N.S. Fatemi and R. Whitehead, Thermochim. Acta, 42 (1980) 323.

3 D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 51 (1981) 269.
4 D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 75 (1984) 59.
5 D. Price, N.S. Fatemi, D. Dollimore and R. Whitehead, Thermochim. Acta, 94 (1985) 313.
6 P.O. Schissel, J. Chem. Phys., 26 (1975) 1276.
7 O. Kaposi, Ann. Univ. Sci. Budapest., XV (1979) 63.
8 O. Kaposi, Acta Chim. Acad. Sci. Hung., 85 (1975) 16.
9 A. Jerez, E. Ramos, M. Gaitán, M.L. Veiga and C. Pico, Thermochim. Acta, 115 (1987) 175.
10 M.M. Romero and J.C. Llópiz, Rev. Cubana Quím., IV (1988) 3.
11 M.M. Romero and J.C. Llópiz, Rev. Cubana Quím., IX (1989) 1.
12 J. Sestak, in Thermophysical Properties of Solids: their Measurements and Theoretical Thermal Analysis, Ed. Acad. Praga, Prague, 1984.
13 V.M. Gorbachev, J. Therm. Anal., 22 (1981) 129.