Thermochimica Acta, 85 (1985) 299—302
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CONTROLLED RATE THERMAL ANALYSIS USING AN INFRA-RED GAS ANALYSER

M. READING and J. ROUQUEROL
C.N.R.S., Centre de Thermodynamique et de Microcalorimétrie, 26 rue du 141ème R.I.A., 13003 Marseille (France)

ABSTRACT

A novel Constant Rate Thermal Analysis apparatus is described and some results for the thermolysis of copper hydroxy carbonate obtained using this apparatus are given.

INTRODUCTION

Constant (or Controlled) reaction Rate Thermal Analysis was first proposed by Rouquerol (ref.1) who has applied this approach to the study of solid state decomposition reactions under vacuum, using either a pressure gauge (Penning or Pirani) or a mass spectrometer as the evolved gas detector. Stacey developed the first constant rate apparatus based on the measurement of gas concentrations in flowing atmospheres (ref.2) using a dew-point hygrometer connected in series with a katharometer. Independently we have developed a similar apparatus which uses two infra-red analysers connected in series (ref.3).

APPARATUS

A schematic diagram of the apparatus is given in Fig.1. The signal from the first gas analyser is maintained constant by controlling the sample temperature, thus assuring that, for a constant flow rate, the rate of evolution of the product gas detected by this gas analyser is maintained constant. The second analyser measures the concentration of a second gas. The length of the furnace ensures that the vector gas, in this case nitrogen, is preheated before reaching the sample. The apparatus was used to study the thermal decomposition of transition metal hydroxy carbonates which evolve carbon dioxide and water simultaneously.

RESULTS

Fig.2 shows some typical results for Merk extra pure copper hydroxy carbonate. The results are expressed as plots of temperature and fraction of total volume of gas evolved (denoted by alpha), for both carbon dioxide and water, against

0040-6031/85/$03.30

time.

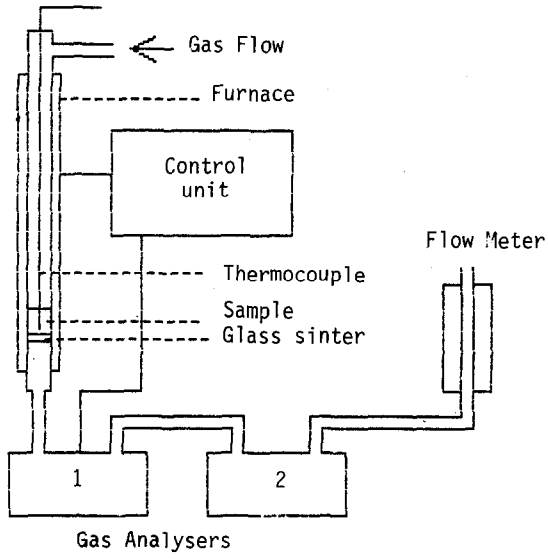

Fig. 1. Schematic diagram of the apparatus.

Carbon dioxide was the gas detected by the first gas analyser, and therefore the gas whose rate of evolution was maintained constant. This is shown by the straight line plot obtained for this gas except over two very small intervals : one at the begining of the experiment, as the constant rate regime was established, and another close to the end of the decomposition. The partial pressure of carbon dioxide was maintained at a value of 1.7 torr. It can be seen that water is evolved simultaneously with the carbon dioxide but not at a constant rate thus the two gases do not follow the same kinetic function.

DISCUSSION

The advantages of this type of experiment are as follows : it shows clearly that, despite the fact that the carbon dioxide concentration remains constant, the two product gases are not evolved at the same rate throughout the decomposition reaction (a rising tenperature experiment would have resulted in the concentrations of both gases changing simultaneously), the rate of decomposition is generally lower than that which can easily be achieved with a rising temperature programme (80% of decomposition occurs in under an hour

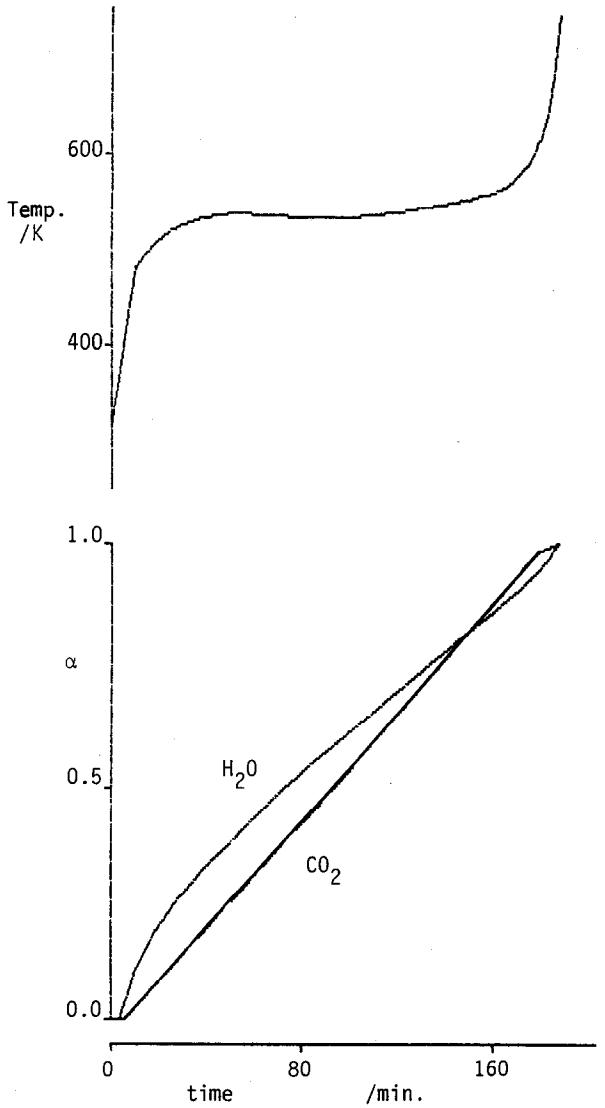

Fig. 2. Results obtained from the thermal decomposition of $Cu_2CO_3(OH)_2$ expressed as plots of (above) temperature and (below) fraction of total volume of gas evolved for both CO_2 and H_2O against time.

using a linear rising temperature programme of 1K/min.) and consequently self cooling effects are reduced, the partial pressure of at least one product gas is maintained at a low value, many gases may be used as the carrier gas (e.g. oxygen, hydrogen or mixtures of gases such as air when a reference gas cell is used), usually the concentrations of any two infra-red active gases may be measured/controlled with a minimum of mutual interference (often difficult to achieve with a mass spectrometer), use of multi-reflection gas cells makes possible experiments over a wide range of pressures. The significance of these results together with other complementary results will be discussed in a future article.

REFERENCES

1 J. Rouquerol, J. Thermal Anal., 2 (1970) 123.
2 M.H. Stacey, Proc. 2nd European Symp. on Thermal Anal., ed. D. Dollimore, Hayden, Aberdeen, (1981) 480.
3 M. Reading, Ph.D Thesis, University of Salford (1983).