Thermochimica Acta, 36 (1980) 343—349

© Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

KINETIC ASPECTS OF THE THERMAL DECOMPOSITION OF ZINC CARBONATE

D. DOLLIMORE, J.A. FRANCE, B.W. KRUPAY and R. WHITEHEAD

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Gt. Britain)

(Received 12 July 1979)

ABSTRACT

The thermal decomposition of zinc carbonate has been studied isothermally at various temperatures between 200 and 260°C. Rising temperature experiments, both thermogravimetry (TG) and differential thermal analysis (DTA), support the formulation of the material studied as $ZnCO_3 \cdot 2\ ZnO \cdot 2\ H_2O$. The decomposition proceeds through the loss of water and then the loss of carbon dioxide in two overlapping stages. The method of utilizing the concept of reduced time indicates only approximate isokinetic character to the decomposition over the temperature range studied. Initial rates of decomposition may be indicative of the rate of loss of water whilst later rates of decomposition may be taken as indicative of the rate of loss of carbon dioxide. The character of the kinetics is deceleratory, but in the region beyond 40% decomposition is approximately linear and due to the loss of carbon dioxide. Ancillary supporting evidence on the mode of decomposition is drawn from surface area measurements and these indicate a loss of area during dehydration and a rise in surface area in the region where carbon dioxide was evolved. The activation energy and pre-exponential term are calculated and possible models for the activated complex considered using the treatment outlined by Shannon. Possible short-comings in the utilization of this data are considered.

INTRODUCTION

The thermal decomposition of solid oxysalts has been the subject of investigations which seek to establish the kinetics of the process and the Arrhenius parameters [1,2]. The kinetics of decomposition of solid oxysalts are largely based on the existence of a reaction interface which may control the rate of reaction [3]. In carbonates, the solid may be reasonably stoichiometric, conform to a simple formula, or show an analysis which indicates a basic formula the exact nature of which depends on the conditions of preparation, and there are many examples which may be cited [4—6]. However, the reaction interface may not be identified with the surface area which also shows changes which are determined by a tendency for the original particles to break up into smaller particles due to the stress imposed through the difference in molecular volumes of the reactant oxysalt and the product metal or oxide [7]. This is opposed by the tendency of all solid particles to sinter under heat treatment [8]. In some well-defined cases it is possible to relate the changes in the surface area with the kinetics of decomposition [9], and it is also possible to relate the changes in surface area to the changes in density between the solid reactant and the solid product [10,11]. The literature on the formula for zinc carbonate shows that various formulae are possible and have been very positively identified [12], but the exact formula probably depends on the conditions of preparation.

EXPERIMENTAL

Material

The zinc carbonate was supplied by an industrial firm with a nominal formula $ZnCO_3 \cdot 2\ ZnO \cdot 3\ H_2O$. A coning and quartering technique was used to obtain a representative sample. The differential thermal analysis (DTA) and thermogravimetry (TG) experiments on this sample, together with chemical analysis, showed that the material could be better formulated as $ZnCO_3 \cdot 2\ ZnO \cdot 2\ H_2O$. Preliminary experiments showed that there was some variation in this formula with the method of preparation and treatment. No significant quantities of other metal ions could be detected.

Apparatus

A Stanton Redcroft Thermobalance TG750 and a Netzsch Model 404 DTA unit with a standard cell were used. The heating rate in both cases was $10°C\ min^{-1}$ in flowing atmosphere of air. Isothermal runs were also made on the TG unit with temperatures chosen so that the time for complete decomposition varied between 30 min and 5 h. A series of zinc carbonate samples were heat treated at given temperatures (1 g of sample heated for 30 min) over a temperature range 100—900° C. The surface areas were measured using equipment relying on the determination of a single nitrogen adsorption point, with the surface area determined by the analytical single point method [13—15]. A further series of samples were prepared by heat treatment at 205° C for various periods of time.

RESULTS

The TG data showed a continuous weight loss between 370 and 560° C, with a maximum rate of weight loss at 450° C. The end product was zinc oxide. The DTA curve gave a broad endothermic peak which corresponded well with the literature data [16,17], the peak extending from 300—520° C, with the peak maxima at 450° C. Isothermal data for zinc carbonate decompositions in air at various temperatures were plotted as $\alpha - t$ (time) plots (Fig. 1). The variation of the surface area with the time of heat treatment of the zinc carbonate in air at 205° C is shown in Fig. 2, while the variation of the surface area with the temperature of heat treatment is given in Fig. 3. The adsorption isotherms analyzed from initial experiments on the decomposed samples of the carbonate were Type 2 on the BET classification, with no indication of a porous structure.

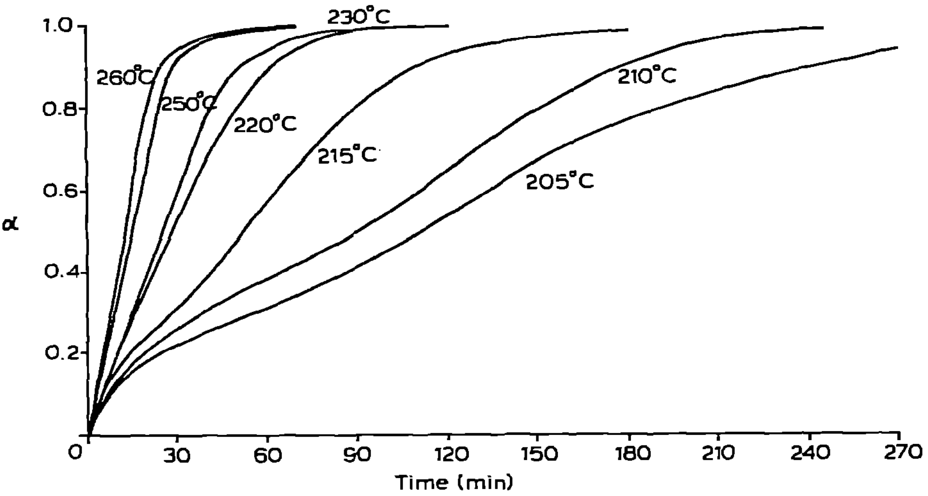
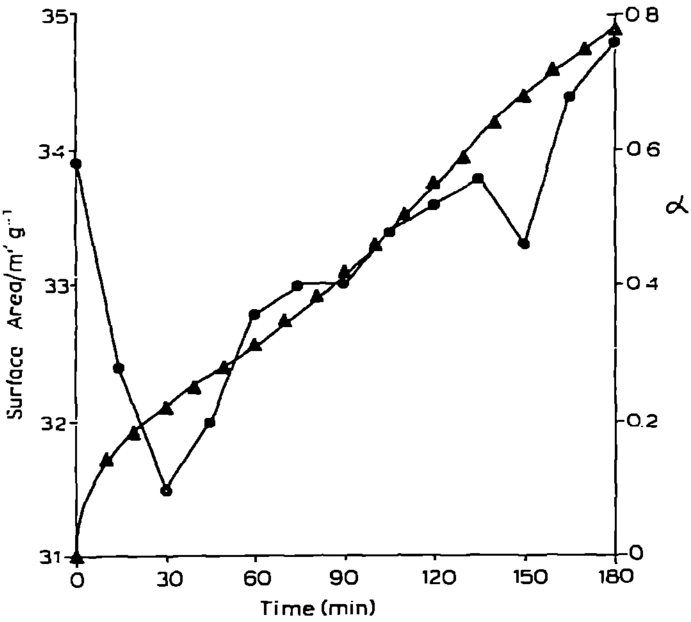


Fig. 1. Isothermal data for zinc carbonate decompositions in air at various temperatures. Ordinate: α(fraction decomposed); abscissa: t(time min^{-1}).



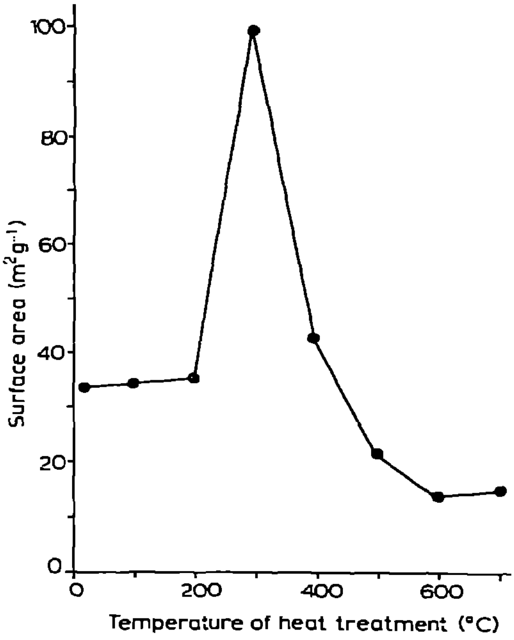


Fig. 2. Variation of the surface area with time of heat treatment of zinc carbonate in air at 205°C. Ordinate: surface area (S m^{-2} g^{-1}), α(fraction decomposed); abscissa: t(time min^{-1}).

Fig. 3. Variation of the surface area with the temperature of heat treatment of zinc carbonate in air. Ordinate: surface area (S m^{-2} g^{-1}); abscissa: temperature of heat treatment (°C).

DISCUSSION

The decomposition of the sample of zinc carbonate ($ZnCO_3 \cdot 2\ ZnO \cdot 2\ H_2O$) showed that it occurred in air in two overlapping stages. At low α (fraction decomposed) values there was more water vapour evolved and at higher α values there was more carbon dioxide evolved. The loss of both water and carbon dioxide was endothermic and the end solid product was zinc oxide. The surface area data (Fig. 2) for isothermal heat treatment indicated that the loss of water accompanied a slight decrease in area, whilst an increase in the surface area was recorded in the region where the loss of the carbon dioxide occurred.

The isothermal data collected in the range 200—260°C (Fig. 1) was only approximately isokinetic in character, as can be seen from the reduced time plot (Fig. 4). This is due to the fact that although the initial rate of decomposition is due mainly to water loss and the later rates due almost entirely to carbon dioxide loss, the α value in each isothermal run at which the water loss was superseded by carbon dioxide was different for each, but beyond $\alpha = 0.65$ the product gas was mainly carbon dioxide. The isothermal data showed that beyond the initial stage a constant or gradually decreasing rate of decomposition occurred. Similar data for other carbonates are shown in Table 1. Formally, a wider distribution of A values might be noted than at first would be acceptable, and part of this may be due to the fact that the reaction rate constant from which this was calculated may not be identified with the specific reaction rate constant that should be used in the Arrhenius equation. It will differ from the true specific reaction rate by a constant factor and, while this will not affect the activation energy (E), it will affect the

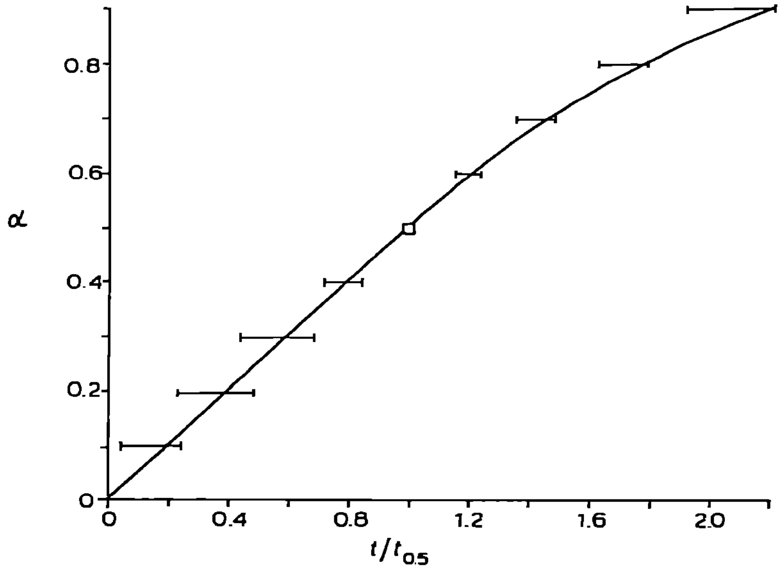


Fig. 4. Reduced time plots for isothermal decomposition of zinc carbonate. Ordinate: α(fraction decomposed); abscissa; $t/t_{0.5}$, where t is the time and $t_{0.5}$ is the time for $\alpha = 0.5$ to be reached.

TABLE 1

Activation energy and pre-exponential factor values for various carbonates

Carbonate	Ref.	Activation energy E (kJ mol^{-1})	Pre-exponential term A (sec^{-1})
Cadmium	5	120	10^8
Manganese		These data on manganese carbonate are characterized by an extreme compensation effect	
Powder	2	94	10^6
Mineral	2	243	10^{22}
In N_2	4	41	10^{20}
In air	4	222	10^{20}
Calcium	18	Some of the data on calcium carbonate and the other carbonates are also quoted by Shannon but with different A values; A values quoted here are taken from original papers	
Vacuo (lump)		146	10^{10}
Vacuo (powder)		176	10^{14}
Magnesium	18	150	10^{11}
Dolomite	18	230	10^{18}
Silver	19	96	10^6
Zinc	20	84	10^5

calculated value of the pre-exponential term (A). There is an additional factor which might be significant in considering the A term, namely that there is some evidence the present investigators have obtained that a common compensation plot can be obtained for some carbonate systems so that an alteration in the value of E is compensated by an appropriate change in the value of A. In solid state decomposition reactions it would seem that some development of the Polanyi—Wigner type of Arrhenius expression as envisaged by Shannon [21] or Cordes [22] would be applicable. The former is perhaps easier to understand, and has the additional advantage of having been applied by that author specifically to carbonates. The specific reaction rate term in solid state decompositions should, however, relate to the movement of the reaction interface, and there is still some doubt whether Shannon, in simply using the first-order decay reaction rate constant, was choosing the correct value. However, again the effect is simply to transpose the values by a constant factor.

Shannon [21] applies the activated complex theory to take into account the various rotational and vibrational degrees of freedom in the activated complex, and the reactant carbonate ion and lattice. He eventually compares the pre-exponential or A factors arising from the two models. The first model he uses assumes that the CO_3^{2-} ion can only torsionally oscillate or librate about its three axes in the carbonate lattice, whilst the second model assumes that it freely rotates about these same axes. The complex is assumed to be approximately a CO_2 molecule freely rotating about the $C \cdots O^{2-}$ axis which is, of course, the reaction co-ordinate. The motion about the other CO^2 rotation axis is taken to be a libration. Certain lattice librations for both the carbonate and oxide lattices are also taken into account.

Comparison of Shannon's predicted values for A with those derived from kinetic data in the cases of calcium carbonate and magnesium carbonate point strongly towards the model which assumes free rotation of the CO_3^{2-} ion. To some extent these conclusions are fortuitous, as the contribution to the partition functions for various "frequencies" as calculated by Shannon are not accurate in a considerable number of instances and are significantly incorrect in a few cases. Also, and more importantly, he takes the temperature for the $MgCO_3$ case to be 600 K, whilst reference to the original experimental paper shows it to be 600° C, i.e. 873 K.

These inaccuracies persuaded us to recalculate all Shannon's partition function values and the resulting pre-exponential factors for the $CaCO_3$ and $MgCO_3$ decompositions, using both 600 and 873 K for the $MgCO_3$ calculations. Corresponding values for zinc carbonate decomposition were also evaluated and the results are quoted below. It is hoped that all these calculations and related discussions will be published in future articles.

The value found here by kinetic experimentation of $E = 94 \pm 9$ kJ mol^{-1} and $A = 1.4 \times 10^6$ sec^{-1} for zinc carbonate decomposition is in reasonable agreement with that reported by Huttig et al. [20]. The theoretical calculations using real and estimated frequency data and the models of Shannon evaluated at the mean experimental (reciprocal) temperature gave

(a) Libration of CO_3^{2-} model

$A = 4.77 \times 10^{12}$ sec^{-1}

and

(b) Free rotation of CO_3^{2-}

$A = 3.63 \times 10^{10}$ sec^{-1}

Obviously, the free rotation model gives a value nearest to the present experimental value, but it is still very considerably greater. It should be noted that the Shannon model assumes all CO_3^{2-} in the sample to be potentially equally active, but if the reaction is only occurring at an interface the experimental value could very possibly be lower by a factor of $\sim 10^4$. It would also seem possible that different positions in the interface would not be identical, and hence produce different results if utilized in the above considerations. The kinetic data, however, would be a reflection of the weighted mean of the contribution from all such sites. The variation resulting from refinements in the calculation taking into consideration these points is, however, uncertain and might only be small. It could provide a possible basis for the compensation effect, but such a suggestion is very speculative at this stage [23,24].

The α vs. t curves were approximately linear over the range $0.2 \leqslant \alpha \leqslant 0.9$, hence the simple but appropriate method of plotting log (rate) against $1/T$ was adopted. This allowed the calculations of the activation energy based on the Arrhenius equation as 94 ± 9 kJ mol^{-1} with the pre-exponential term (A) calculated as 1.4×10^6 sec^{-1}, with upper and lower limits of 1.3×10^7 and 1.5×10^5 sec^{-1}, respectively.

The surface area data must not be confused with the reaction interface area, but although changes in the surface area can be noted, i.e. the presence of water vapour caused a slight sintering effect, whilst the production of carbon dioxide caused a slight increase in area, the change in surface area in the isothermal experiment studied is very small and for practical purposes can be regarded as constant (Fig. 2). On the assumption that the kinetics are based on the rate of growth of a reaction interface, then the almost linear plots of $\alpha \sim t$ in the region studied suggest a constant area reaction interface as well. This implies a particle structure which can allow growth of the reaction interface through the body of the solid without appreciable alteration in the area, e.g. plate-like particles, but there are several alternative shapes which would produce the same phenomena. The constant surface area measurements mean that surface area destroyed through the decomposition of zinc carbonate is compensated by the fresh area generated in the product zinc oxide. The presence of a peak in the plot of surface against temperature (Fig. 3), however, provides evidence that the strains imposed by the decomposition are temperature dependent and that the variations in the relative distribution of sites of differing energy taking place in the chemical decomposition process at the reaction interface can be quite wide and dependent upon external conditions.

REFERENCES

1 J.H. Sharp, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol. 2, Academic Press, London, 1972, p. 47.
2 R.I. Razouk, R.Sh. Mikhail and G.M. Habashy, Egypt. J. Chem., 1 (1958) 223.
3 P.W.M. Jacobs and F.C. Tomkins, in W.E. Garner (Ed.), Chemistry of the Solid State, Butterworths, London, 1955, Chap. 7, pp. 184—212.
4 D. Dollimore and K.H. Tong, in G.M. Scwab (Ed.), Proc. 5th Int. Symp. Reactivity Solids, Munich, Elsevier, Amsterdam, 1964, p. 497.
5 R.Sh. Mikhail, D. Dollimore, A.M. Kamel and N.R. El-Nazer, J. Appl. Chem. Biotech., 23 (1973) 419.
6 P.K. Gallagher and D.W. Johnson, Thermochim. Acta, 14 (1976) 255.
7 D. Dollimore and D. Nicholson, J. Chem. Soc., (1962) 960.
8 D. Dollimore and P. Spooner, Trans. Faraday Soc., 67 (1971) 2750.
9 D. Dollimore and D. Tinsley, J. Chem. Soc. A, (1971) 3043.
10 D. Dollimore and J. Pearce, J. Therm. Anal., 6 (1974) 321.
11 D. Dollimore and D.V. Nowell, Thermal Analysis, Proc. 4th ICTA, Budapest, Vol. III, 1974, p. 63.
12 J.R. Partington, General and Inorganic Chemistry, MacMillan, London, 1946, p. 388.
13 D. Dollimore, P. Spooner and A. Turner, Surf. Technol., 4 (1976) 121.
14 A.L. Klyacho-Gurvich, Izv. Akad. Nauk S.S.S.R., Otd. Khim., (1961) 1884 [English Translation, (1961) 1756].
15 D. Dollimore and P. Spooner, J. Appl. Chem. Biotech., 24 (1974) 35.
16 C.W. Beck, Am. Mineral., 35 (1950) 985.
17 C.L. Cuthbert and R.A. Rowland, Am. Mineral., 32 (1947) III.
18 H.T.S. Britton, S.J. Gregg and G.W. Windsor, Trans. Faraday Soc., 48 (1952) 63, 70.
19 W.D. Spencer and B. Topley, J. Chem. Soc., (1929) 2633.
20 G.F. Huttig, J.W. Mellor and G. Lehmann, Z. Phys. Chem., Abt. B, 19 (1932) 1.
21 R.D. Shannon, Trans. Faraday Soc., 60 (1964) 1902.
22 H.F. Cordes, J. Phys. Chem., 72 (1968) 2185.
23 D. Dollimore and P.F. Rodgers, Thermochim. Acta, 30 (1979) 273.
24 D. Dollimore, G.R. Heal and B.W. Krupay, Thermochim. Acta, 24 (1978) 293.