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The application of constant rate thermal analysis to the study of the thermal decomposition of copper hydroxy carbonate

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Abstract

The thermal decomposition of copper hydroxy carbonate was examined using conventional rising temperature thermogravimetry and constant rate thermal analysis (CRTA). The low-pressure CRTA results showed that the two product gases, water and carbon dioxide, are evolved at different rates throughout the decomposition. A CRTA apparatus using infrared gas detectors was able to measure and control the evolution of these two gases independently and established that more water is evolved at the start of the reaction and more carbon dioxide near the end. The kinetics of the reaction were investigated using both rising temperature and CRTA results and reasonable agreement was found for the activation energy. However, the results for the reaction mechanism proved inconclusive. The development of the surface area as a function of the extent of reaction was investigated and found to be markedly non-linear. This fact is discussed in relation to the evolved gas results and a previously proposed mechanism for solid state decomposition reactions.

INTRODUCTION

This article considers the decomposition of copper hydroxy carbonate. The interest in this reaction arises because the decomposition of this material is a route to copper oxide with a high surface area and, consequently, good properties as a catalyst. This compound has received very little attention. Zivkovic et al. [1] concluded that the reaction may be expressed as

$$Cu_2CO_3(OH)_2 \rightarrow 2CuO + CO_2 + H_2O$$

Using rising temperature thermogravimetry, they determined the activation energy as 71 ± 27 kJ mol^{-1} [1]. In a subsequent study using differential thermal analysis results, they found a value of 62 ± 27 kJ mol^{-1} [2]. In both cases the experiments were carried out under flowing air.

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In previous articles we and others have demonstrated the advantages of constant rate thermal analysis for the study of thermal decomposition reactions [3-5]. We have also described a novel CRTA apparatus [6] ideally suited for the study of compounds like copper hydroxy carbonate which evolve more than one gas simultaneously when decomposing. It is also designed to allow the subsequent characterisation of the catalytic properties of the decomposition product in situ and/or the study of the activation of the catalyst using reactive atmospheres. Here we use this and other methods, including the use of adsorption isotherms, to characterise both the physical and chemical changes that occur during this reaction.

EXPERIMENTAL

All but one of the results presented in this section were obtained using Prolabo reagent-grade copper hydroxy carbonate. The X-ray powder diffraction pattern showed the sample to be poorly crystalline; however four peaks were discernible and agree with the ATMS standard. In one case, Merck extra-pure copper hydroxy carbonate was used, again the powder X-ray diffraction pattern showed that the compound was poorly crystalline; however, four peaks were discernible and agree with the ATMS standard. Data for both samples together with the ATMS standard are given in Table 1.

The TGA measurements under flowing atmospheres were made using a Stanton Redcroft TG750. The vacuum CRTA measurements were made using a modified Mettler Thermoanalyser No. 76 [7] adapted by Rouquerol to carry out controlled rate experiments. Similarly, samples prepared for surface area measurements were prepared using a CRTA also developed by Rouquerol [8]. Surface areas were measured using the BET method applied

TABLE 1

ATMS and found X-ray diffraction data for $Cu_2CO_3(OH)_2$

ATMS [a]		Prolabo		Merck	
d/Å	I/I_1	d/Å	I/I_1	d/Å	I/I_1
5.99	55				
5.06	75	5.08	50	5.08	47
3.69	85	3.70	62	3.70	53
2.86	100	2.87	100	2.87	100
2.82	40				
2.78	45	2.79	55		
2.52	55	2.52	46	2.52	39

[a] All $I/I_1 \leqslant 30$ excluded.

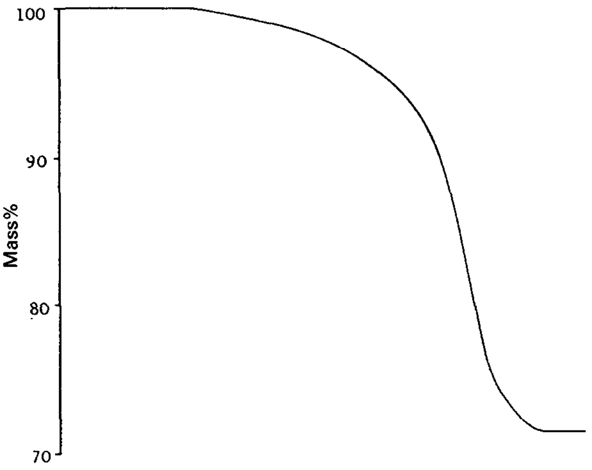

Fig. 1. Rising temperature results for $Cu_2CO_3(OH)_2$ under flowing nitrogen.

to nitrogen adsorption isotherms measured using a slow continuous gas introduction technique [9]. CRTA measurements under flowing atmospheres were carried out using an apparatus developed by us [6].

RESULTS

The results from a rising temperature experiment using a 10 mg sample (Prolabo) carried out at a heating rate of $1.667°C\,min^{-1}$ under flowing nitrogen at $100\,ml\,min^{-1}$ using the Stanton Redcroft TG 750 are given in Fig. 1. The total weight loss was 28.7% which corresponds exactly with the theoretical weight loss for the reaction

$$Cu_2CO_3(OH)_2 \rightarrow 2CuO + CO_2 + H_2O$$

The results of a vacuum constant rate thermal analysis experiment using a 96.4 mg sample (Prolabo) at a regulated pressure of 5×10^{-5} Torr are given in Fig. 2; the total weight loss was found to be 28.8%. The results are expressed as temperature and percentage weight loss against time.

The reaction was timed from the beginning of constant rate regulation. Before this point, there was a small weight loss while a constant rate regime was established; thus the weight loss at $t = 0$ is not zero. Careful inspection of the weight loss curve shows that it is not linear. This is explained by the fact that the Penning gauge used as part of the control loop to maintain constant gas pressure (and thus, under the conditions of the experiment, a nominal constant rate of weight loss) has different sensitivities to different gases; thus, the ratio of evolution of H_2O and CO_2 is not constant throughout the course of the decomposition. This fact prompted the development of the constant-rate apparatus described in ref. 6 which is capable of regulating the partial pressure of one gas while simultaneously monitoring the evolution of

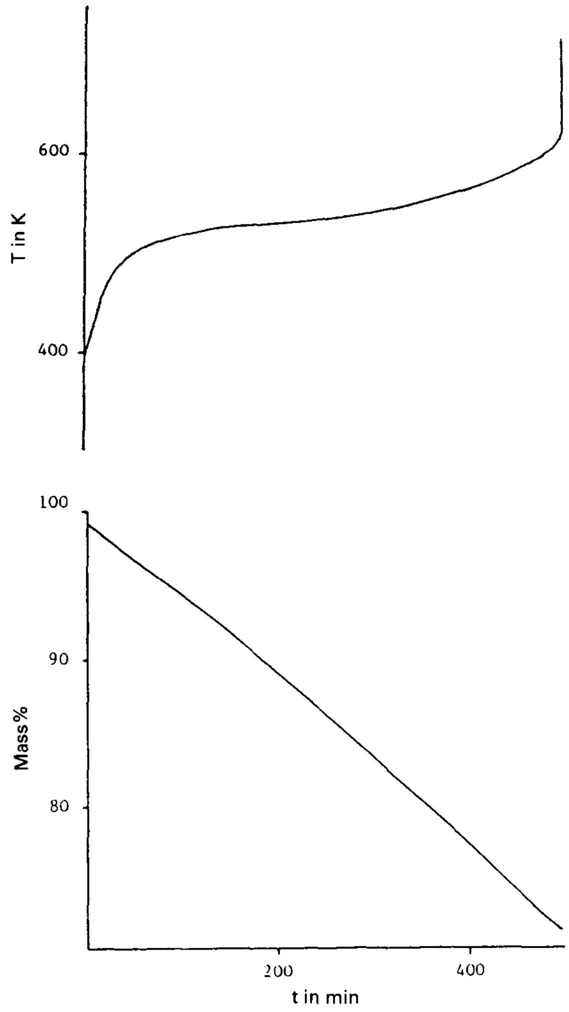

Fig. 2. Constant rate results for 96.4 mg $Cu_2CO_3(OH)_2$ at a regulated pressure of 5×10^{-5} Torr.

the other. The results from a constant rate thermal analysis experiment carried out under flowing nitrogen at a regulated CO_2 partial pressure of 1.7 Torr using a flow rate of 160 ml min^{-1} and a sample size of 740 mg (Prolab) are given in Fig. 3.

The results are expressed as plots of temperature and α for both CO_2 and H_2O against time. It can clearly be seen that H_2O and CO_2 are evolved at different rates throughout the decomposition; thus the vacuum result is confirmed. The two gases, therefore, follow different kinetic functions. To investigate whether this phenomenon was peculiar to the Prolabo sample, a further experiment was carried out using the Merck extra-pure copper hydroxy carbonate. The experiment was conducted under the same experi-

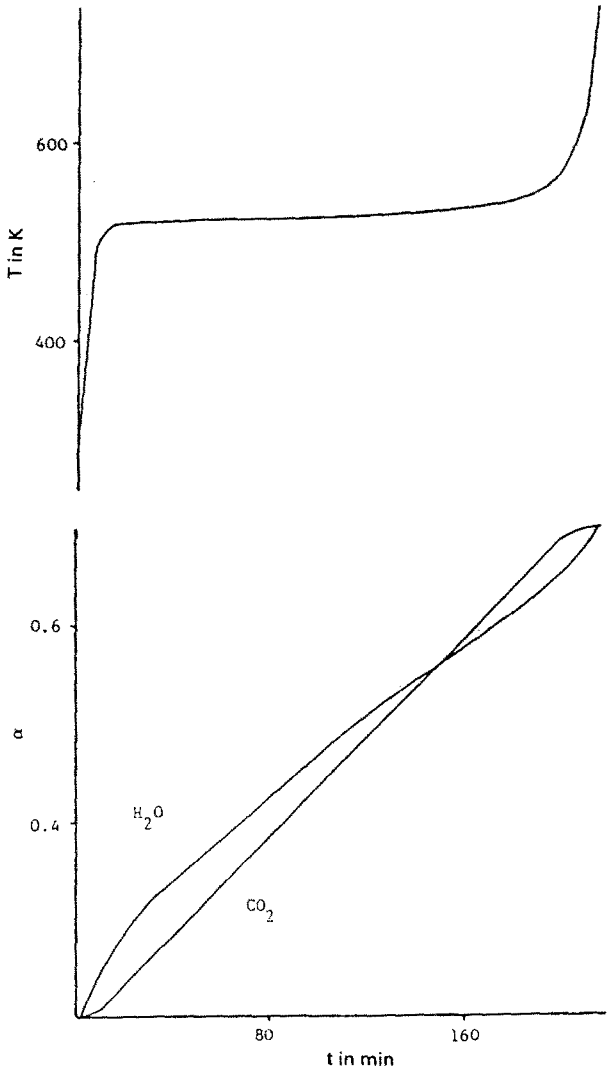

Fig. 3. Constant rate results (w.r.t. CO_2) for 740 mg $Cu_2CO_3(OH)_2$ under flowing nitrogen at 160 ml min^{-1}, regulated CO_2 partial pressure 1.7 Torr (Prolabo).

mental conditions as those given above for the Prolabo sample except that a sample size of 626 mg was used; the results are given in Fig. 4. It can be seen that the results are similar to those given in Fig. 3.

Activation energy measurements

The results of a series of rising temperature experiments using a 10 mg sample (Prolabo) under nitrogen flowing at 100 ml min^{-1} at a heating rate of 1.6, 2.5, 3.8 and 5.9°C min^{-1} carried out on the Stanton Redcroft TG 750

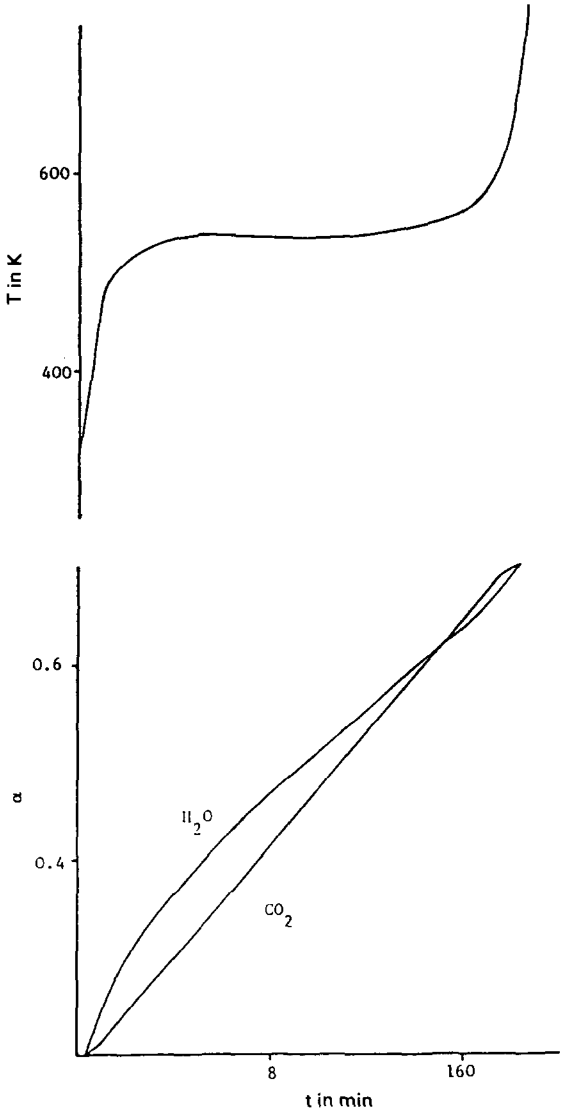

Fig. 4. Constant rate results (w.r.t. CO_2) for 626 mg $Cu_2CO_3(OH)_2$ under flowing nitrogen at 160 ml min^{-1}, regulated CO_2 partial pressure 1.7 Torr (Merck).

are given in Fig. 5. The kinetic analysis used is that given in ref. 3. No assumption about the alpha function is made and the activation energy is measured as a function of extent of reaction at intervals of 0.1 fraction reacted; the results are given in Table 2. There is some evidence of an increasing trend in E as the reaction proceeds but the scatter in the results makes this very uncertain. The average value from Table 2 is 193 kJ mol^{-1} with a standard deviation of 13.7. A rate jump constant rate thermal analysis experiment [3] was carried out using a sample size of 300 mg

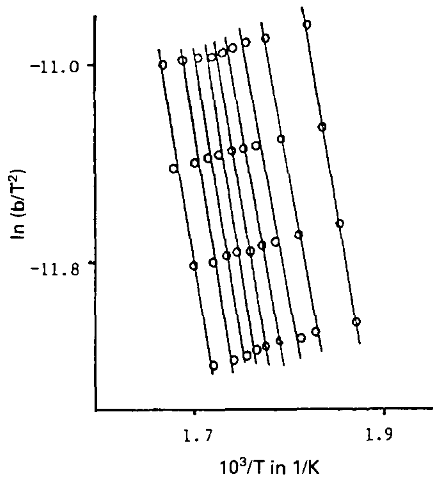

Fig. 5. Rising temperature results for 10 mg $Cu_2CO_3(OH)_2$ under flowing nitrogen at 100 ml min^{-1}.

TABLE 2

Activation energies from Fig. 5

a	E/kJ mol^{-1}	E_i/kJ mol^{-1}	r
0.1	184	184	0.987651
0.2	177	177	0.991108
0.3	169	170	0.967361
0.4	192	192	0.983138
0.5	209	209	0.987667
0.6	212	212	0.987681
0.7	200	201	0.983196
0.8	203	204	0.983219
0.9	193	194	0.983221

(Prolabo) and a regulated pressure of 5×10^{-5} Torr involving 19 rate jump measurements. Again this method [3] makes no assumptions about the form of the alpha function and measures E as a function of extent of reaction. The value obtained was 170 kJ mol^{-1} with a standard deviation of 21.0 with no clear trend of increasing or decreasing with extent of reaction. As observed above, the rate of mass loss is not constant throughout the decomposition for this compound. However, over the narrow range of α considered at each rate jump, the reaction rate may be considered to be a very close approximation to constant. The agreement between the activation energy found under flowing nitrogen and the value found under vacuum, 193 and 170 kJ mol^{-1} respectively, is reasonable.

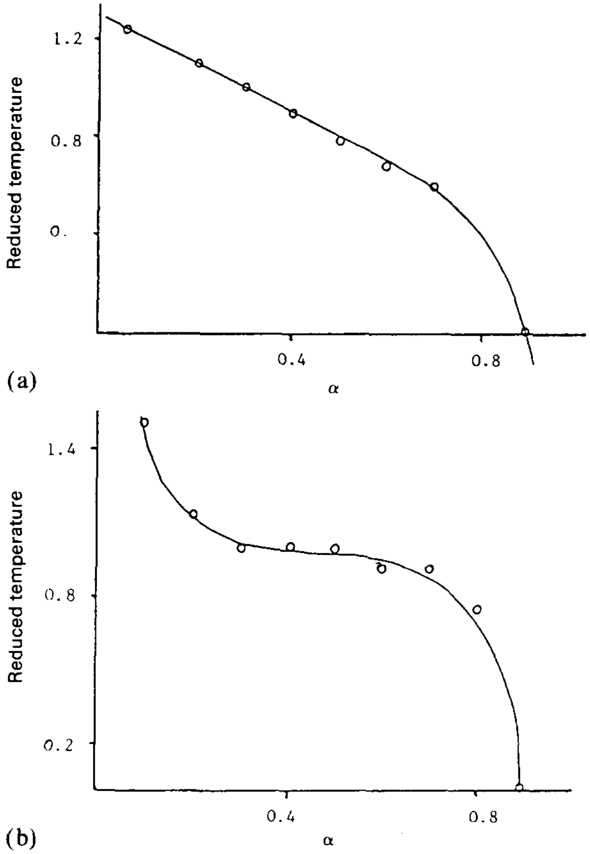

Fig. 6. Reduced temperature plots for CO_2 evolution. (a) Prolabo sample from Fig. 3. (b) Merck sample from Fig. 4.

The alpha function

Given that the two evolved gases apparently follow different kinetic functions, no meaningful analysis can be made using the mass loss data. Reduced temperature plots [4] from the two constant rate thermal analysis (constant rate with respect to the evolution of CO_2) experiments carried out under flowing nitrogen, see Figs. 3 and 4, are given in Fig. 6a and 6b for the Prolabo and Merck samples respectively. It can be seen that there are considerable differences between the two plots. The results from ref. 5 on calcium carbonate suggest that fitting experimental data to idealised models is perhaps not a very meaningful exercise. This would seem to be especially true when simply changing the source of the sample can change the apparent α function so markedly. However, in the case of calcium carbonate it was found that the type of mechanism was consistent even if the detailed function appeared to change with experimental conditions. Here the Prolabo sample gives a reduced temperature plot indicative of an order expression whereas the Merck sample is closer to a diffusion-limited equation [4].

Surface area measurements

A sample of 3436.75 mg (Prolabo) was decomposed using the constant rate thermal analysis equipment described in ref. 8 at a regulated pressure of 5×10^{-3} Torr for CO_2. In this apparatus a Pirani gauge is used which also has different sensitivities to different gases; the reaction rate was therefore not truly constant, and the gauge was calibrated against air. At intervals, the surface area of the sample was measured using the low-temperature nitrogen adsorption apparatus described in ref. 9. The BET plots used to determine the surface areas are given in Fig. 7. The surface areas with the corresponding weight losses are given in Table 3. The surface areas with respect to the starting weight are plotted against percentage weight loss in Fig. 8. The markedly non-linear relationship between the extent of decomposition and the surface area is probably a reflection of the fact that during the early part of the decomposition reaction, more water is evolved than carbon dioxide, see Fig. 3. This would suggest that water loss is associated with a greater surface area increase than carbon dioxide. This, together with the fact that the pressures of the evolved gases change over the course of the decomposition, which may affect the development of the surface area, combine to make the relationship between surface area and extent of decomposition a complex one.

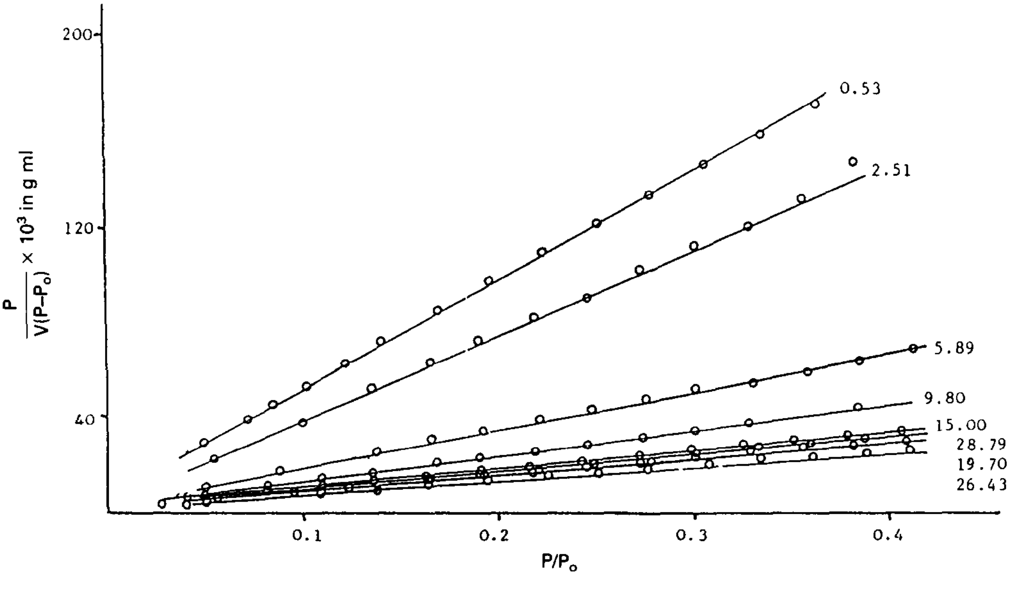

Fig. 7. BET plots for $Cu_2CO_3(OH)_2$.

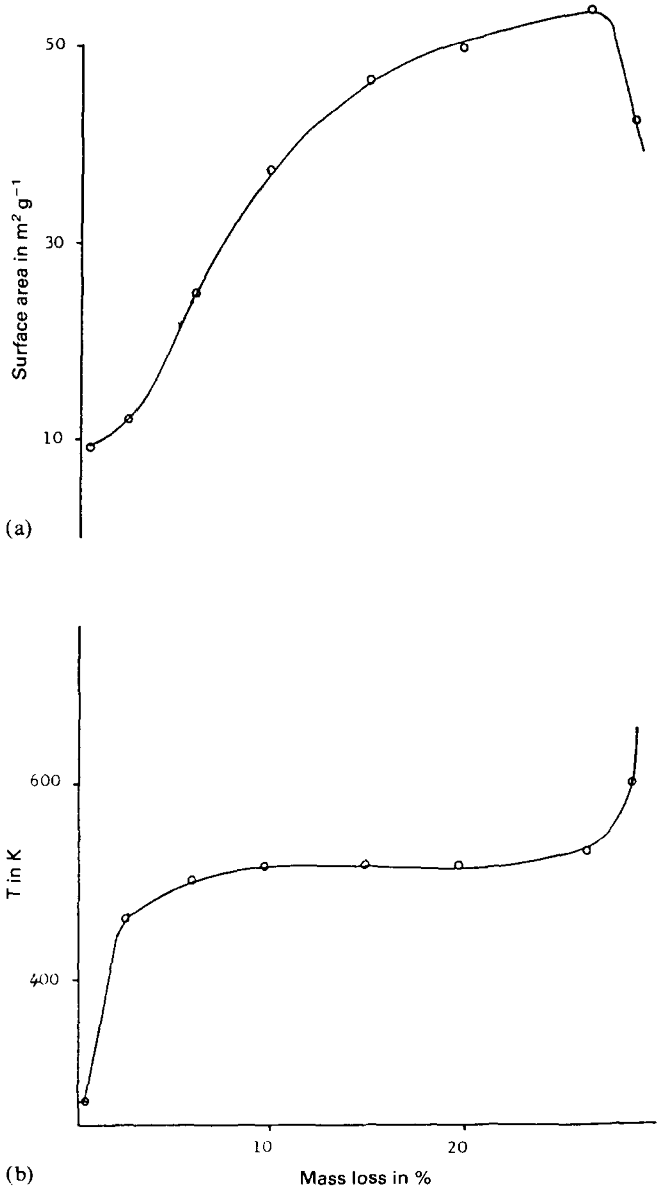

Fig. 8. (a) Surface area changes with extent of decomposition for $Cu_2CO_3(OH)_2$. (b) CRTA temperature trace.

DISCUSSION OF RESULTS

The activation energies given above are overall values for the loss of both water and carbon dioxide. It is interesting to note that the fact that the two product gases are not evolved at the same rate during the decomposition does not apparently give rise to greatly different activation energies over

TABLE 3

Surface area measurements for decomposing copper hydroxy carbonate

Wt. loss/%	Surface area/ ($m^2 g^{-1}$)	*C*	Surface area w.r.t. starting weight
0.53	9.4	73	9.4
2.51	12.1	107	11.9
5.89	26.5	77	25.1
9.80	41.3	44	37.5
15.00	54.4	58	46.5
19.70	61.2	79	49.5
26.43	72.9	57	54.0
28.79	58.9	71	42.3

different ranges of α. Despite the fact that the kinetics of the loss of the two product gases do not follow the same $f(\alpha)$, it would seem unlikely that they are evolved independently of one another. We have previously proposed that the interface should be considered to have a certain thickness [5]. Here we could envisage that through this thickness there would be gradients of concentrations for the hydroxide, carbonate and the product oxide. In the early stages of the reaction, the interface must be richer in carbonate; then, during the latter stages, richer in hydroxide. The crossover point comes at about $\alpha = 0.6$ and it is perhaps significant that this corresponds to the point at which there is a dramatic reduction in the rate of rise of the growth in surface area.

This study can only serve as a preliminary investigation into what is a complex system. Further work is clearly required before a detailed understanding of this reaction can be achieved. The results presented here should serve as a useful reference and an illustration of the value and future potential of the apparatus we have developed [6].

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