

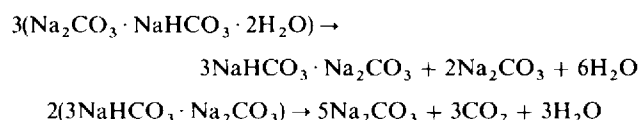
Thermal Decomposition of Solid Sodium Sesquicarbonate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$

Matthew C. Ball,* Christine M. Snelling, Alec N. Strachan and Rebecca M. Strachan

Department of Chemistry, University of Technology, Loughborough, Leicestershire, LE11 3TU, UK

The thermal decomposition of solid sodium sesquicarbonate has been studied at temperatures between 350 and 487 K in nitrogen and carbon dioxide atmospheres. In nitrogen, a single-stage decomposition to sodium carbonate occurs, following Avrami–Erofev kinetics ($n = 2$), with an inflexion at ca. 390 K. The activation energies are 24 kJ mol⁻¹ for the high-temperature region and 58 kJ mol⁻¹ for the low-temperature region. In carbon dioxide above 435 K, the single-stage reaction follows contracting disc kinetics with an activation energy of 29 kJ mol⁻¹. In carbon dioxide at low temperatures, wegscheiderite ($\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$) and sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) are formed, and this reaction follows first-order kinetics, with an activation energy of 67 kJ mol⁻¹. Microscopic evidence is also presented. Relationships between the decomposition of sesquicarbonate and other related compounds are discussed.

Relatively little work has been carried out on the thermal decomposition of sodium sesquicarbonate despite its importance relative to sodium hydrogencarbonate as a source of sodium carbonate.¹ Vapour pressure measurements have been carried out^{2–4} and interpreted in terms of a reaction mechanism,^{3,5} enthalpy of solution measurements have also been made.⁶ A DTA curve for the compound was determined by Beck,⁷ as part of an extensive study of carbonate decompositions, but no interpretation was attempted. The fullest study has been carried out by Gancy,³ who measured equilibrium vapour pressures and suggested the following two-stage decomposition scheme:



The intermediate, wegscheiderite, is naturally occurring. Gancy suggests that it can be formed when carbon dioxide reacts with sesquicarbonate.³ The crystal structure of sesquicarbonate has been determined;⁸ the unit cell is monoclinic, space group C2/c, with dimensions $a_0 = 2.0346$ nm, $b_0 = 0.349$ nm, $c_0 = 1.0296$ nm, $\beta = 106^\circ 26'$, $Z = 4$. Each sodium ion is coordinated by six oxygen atoms, Na(1) by oxygens from carbonate ions, while Na(2) has four oxygens from carbonate ions and two from water molecules. These water molecules lie in sheets between layers made up of pairs of hydrogen-bonded carbonate ions linked by sodium ions.

The work described here studies the effects of nitrogen and carbon dioxide at atmospheric pressure on the decomposition stoichiometry and kinetics.

Experimental

The sesquicarbonate used was supplied by ICI (Chemicals and Polymers). It gave an X-ray diffraction pattern in excellent agreement with that published.⁹ The loss in mass on ignition was in good agreement with that required for the formation of sodium carbonate (observed: 29.6%, theory: 29.65%). The decomposition studies were carried out using a C.I. Microforce balance Mark 2C and potentiometric recorder. Sample masses of 10 mg \pm 10% were used throughout, allowing a recorder sensitivity of 4 mg f.s.d. Isothermal temperatures were probably accurate to ± 1 K. Nitrogen (99.9%) or carbon dioxide (99%) were passed over the sample at a rate of 5 cm³ min⁻¹. For mixtures, the gases were metered separately and the total flow controlled to the same

rate. The humidity of the gas stream was controlled by passing the gas over drying agents (silica gel followed by magnesium perchlorate). The starting material and reaction products (decomposed to varying extents) were examined by SEM (ISI SS40). The surface area of the fully decomposed product was measured by nitrogen sorption (B.E.T. method). The surface area of the starting material was too low to be measured in this way, so estimates were made from micrographs.

Results

Mass Losses

All runs carried out under nitrogen, and those at temperatures above 435 K under carbon dioxide, showed a single-stage mass loss of 29.6%; those runs carried out at temperatures below 410 K in carbon dioxide showed a three-stage loss of 10.6, 16 and 29.6% (cumulative losses). At higher temperatures the 16% plateau disappeared, giving a two-stage decomposition.

Reaction Mechanisms

The results for all runs were analysed by the method of reduced-time plots, based on the time for 50% reaction.¹⁰ Comparison of the experimental data with equations for nucleation and growth, phase boundary or diffusion control of the reaction allowed a decision to be made on the most likely rate-controlling steps.

Single-stage Decomposition

Nitrogen Atmosphere, Whole Temperature Range. Over the temperature range studied (350–487 K) a single mechanism appeared to be rate controlling. The best fit between experimental and model reduced-time plots was in terms of Avrami–Erofev kinetics with $n = 2$, following the equation $-\ln(1 - \alpha) = kt^2$. Typical comparisons between experimental and model curves are shown in Fig. 1. An Arrhenius plot using the derived rate data is shown in Fig. 3 (later).

Carbon Dioxide, High Temperatures. Above 435 K, at which temperature the reaction becomes single stage, the best fit between experimental and model data was in terms of the contracting disc equation, $1 - (1 - \alpha)^{1/2} = kt$. The reaction rates in carbon dioxide were lower than those in nitrogen. Typical comparisons are shown in Fig. 2, and the rate data are incorporated into Fig. 3. Activation energies and frequency factors derived from Fig. 3 are shown in Table 1.

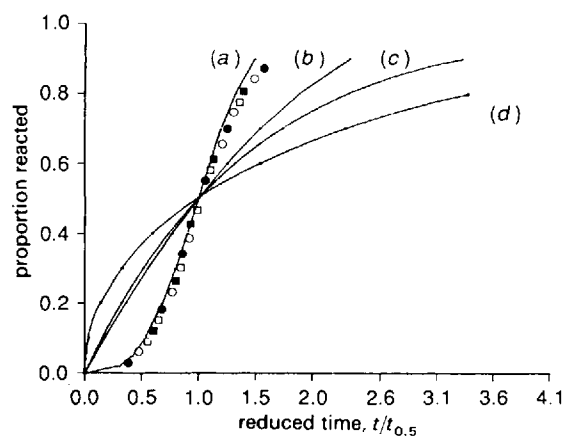


Fig. 1 Reduced time plot for the decomposition of sodium sesquicarbonate in nitrogen: (a) Avrami-Erofev equation, $n = 2$; (b) first-order equation; (c) contracting disc equation; (d) Ginstling-Bronshstein diffusion equation. ●, 361; ■, 375; ○, 421; □, 460 K

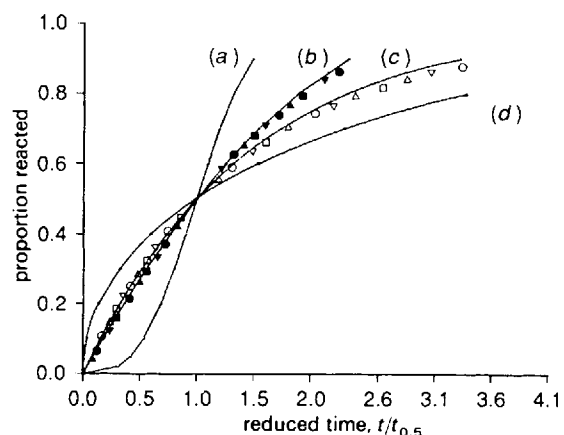


Fig. 2 Reduced time plot for the decomposition of sodium sesquicarbonate in carbon dioxide: (a) Avrami-Erofev equation, $n = 2$; (b) first-order equation; (c) contracting disc equation; (d) Ginstling-Bronshstein diffusion equation. ●, 427; ■, 417; ▼, 411; ▲, 395; ○, 487; □, 475; ▽, 455; △, 444 K

Multi-stage Decomposition in Carbon Dioxide at Low Temperatures

The following kinetic description refers to the first stage in the decomposition, since the mass losses outlined earlier made it clear that the second and third stages refer to the decompositions of monohydrate and wegscheiderite, respectively, and these have already been studied.^{11,12} The temperature range over which this first stage was studied was 385–427 K, and the best fit between experimental and model data was in terms of first-order kinetics, following the equation $-\ln(1 - \alpha) = kt$. Typical results are shown in Fig. 2. The Arrhenius plot is included in Fig. 3 and the derived data are contained in Table 1. The transition between the one-stage

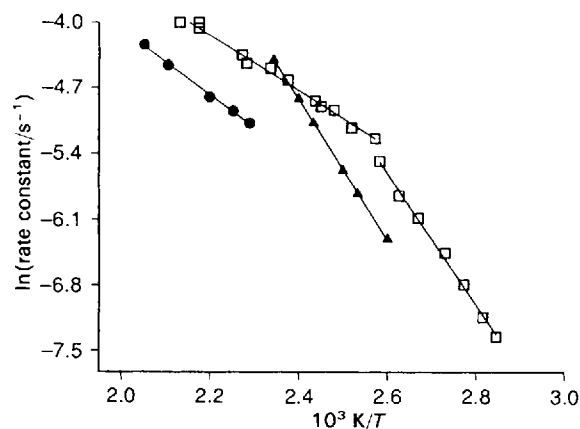


Fig. 3 Arrhenius plot for the decomposition of sodium sesquicarbonate: □, nitrogen; ▲, carbon dioxide, first order; ●, carbon dioxide, contracting disc

and three-stage reactions was studied at 407 K as a function of partial pressure of carbon dioxide. The nitrogen content was varied between 6 and 96%. The number of stages changed between 18 and 25% nitrogen. Typical results are shown in Fig. 4.

Surface Area Measurements

The estimated surface area of the original sesquicarbonate was $0.1 \text{ m}^2 \text{ g}^{-1}$, while the sodium carbonate product had a measured area of $2.93 \text{ m}^2 \text{ g}^{-1}$.

SEM Observations

Samples were heated at 390 and 450 K in both nitrogen and carbon dioxide atmospheres to varying degrees of decomposition before being examined in the scanning electron micro-

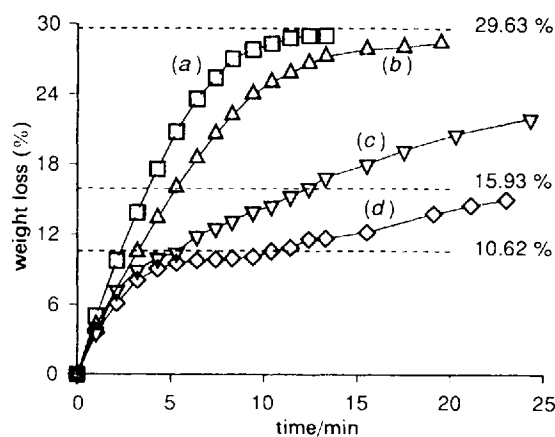


Fig. 4 Effect of atmosphere composition on weight loss: (a) 96, (b) 42, (c) 23, (d) 15% N_2

Table 1 Arrhenius parameters for the decomposition of sodium sesquicarbonate

atmosphere	temperature range/K	products	best-fit mechanism ^a	activation energy/ kJ mol^{-1}	frequency factor ($\log A$)
nitrogen	390–460	Na_2CO_3	A2	24	1.1
	350–390	Na_2CO_3	A2	58	5.4
carbon dioxide	435–487	Na_2CO_3	R2	29	3.0
	385–420	wegscheiderite and monohydrate	F1	67	6.0

^a A2, Avrami-Erofev kinetics: $-\ln(1 - \alpha)^{1/2} = kt$. R2, contracting disc kinetics: $1 - (1 - \alpha)^{1/2} = kt$. F1, first-order kinetics: $-\ln(1 - \alpha) = kt$.

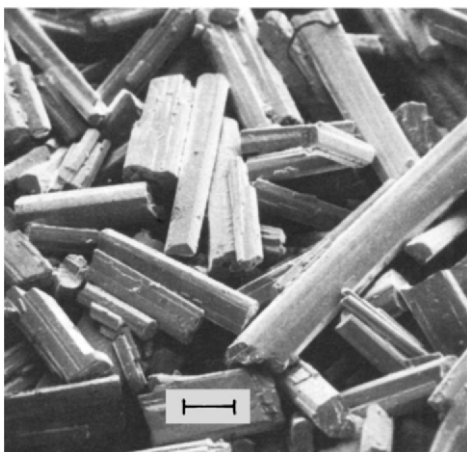


Fig. 5 Starting material, as received, bar = 200 μm

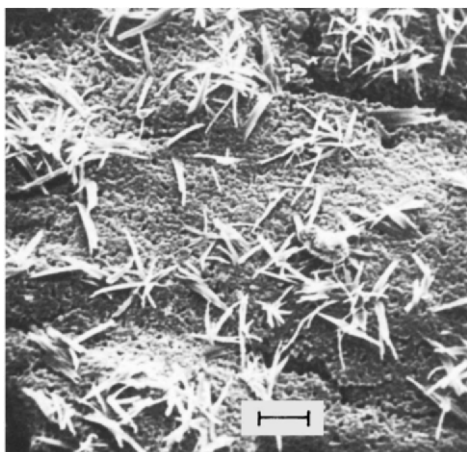


Fig. 6 $T = 450 \text{ K}$, $\alpha = 1.0$, nitrogen, bar = 5 μm

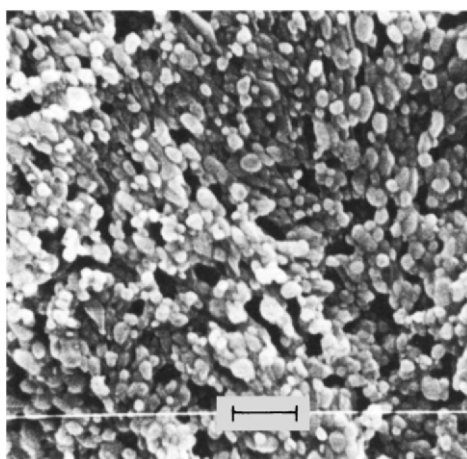


Fig. 7 $T = 450 \text{ K}$, $\alpha = 1.0$, carbon dioxide, bar = 1 μm

scope. These temperatures were chosen to lie in the high- and low-temperature regions identified in the kinetic studies.

The starting material was well crystallised, with smooth faces (Fig. 5). High-temperature decomposition in nitrogen produced uniformly porous sodium carbonate with outgrowths (Fig. 6). These outgrowths, while not uncommon, were not uniformly spread across the crystal surface.

High-temperature decomposition in carbon dioxide produced porous sodium carbonate without outgrowths (Fig. 7). Longer heating times in carbon dioxide gave evidence of recrystallisation not shown by samples heated in nitrogen (Fig. 8).

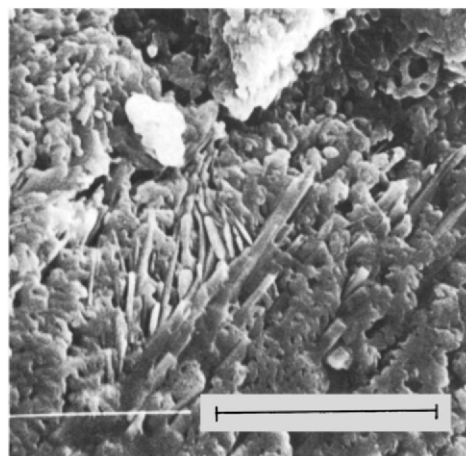


Fig. 8 $T = 450 \text{ K}$, $\alpha = 1.0$, carbon dioxide, bar = 10 μm

Low-temperature heating in nitrogen generated large numbers of two-dimensional nuclei (Fig. 9) within which needles of a second phase could be seen (Fig. 10). At longer times and higher α values, a limited number of these grew, developed porosity and showed orientation with the long axis of the original crystals (Fig. 11). In carbon dioxide, at low temperatures, nuclei could again be seen, but their appearance was not the same as those produced in nitrogen. They were larger and more widely spread (Fig. 12), and did not contain any obvious second phase (Fig. 13). Longer heating

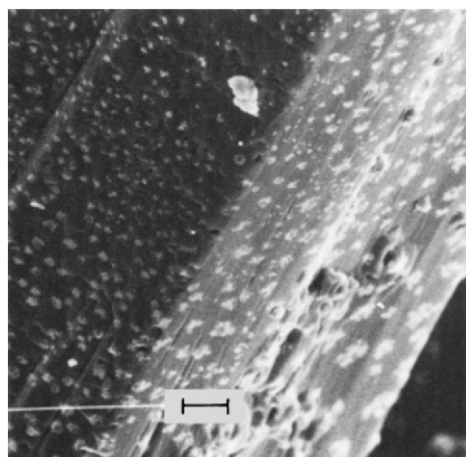


Fig. 9 $T = 390 \text{ K}$, $\alpha = 0.01$, nitrogen, bar = 10 μm

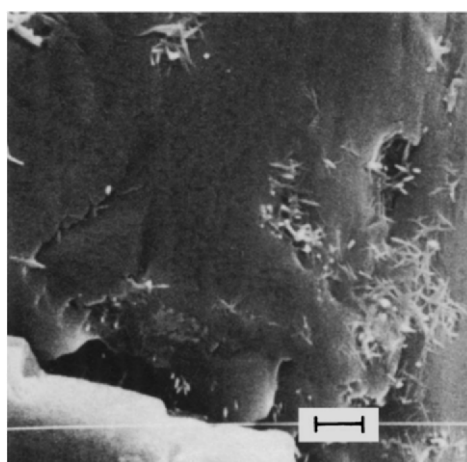


Fig. 10 $T = 390 \text{ K}$, $\alpha = 0.01$, nitrogen, bar = 1 μm

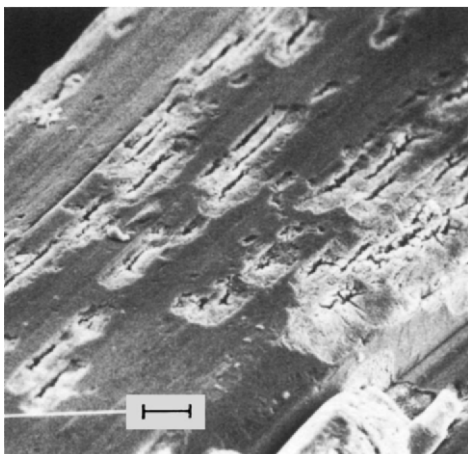


Fig. 11 $T = 390\text{ K}$, $\alpha = 0.1$, nitrogen, bar = $10\ \mu\text{m}$

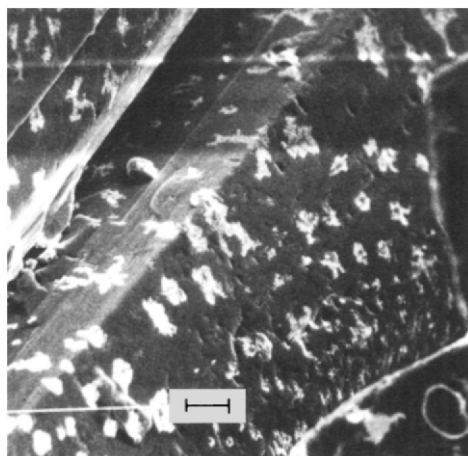


Fig. 12 $T = 390\text{ K}$, $\alpha = 0.01$, carbon dioxide, bar = $10\ \mu\text{m}$

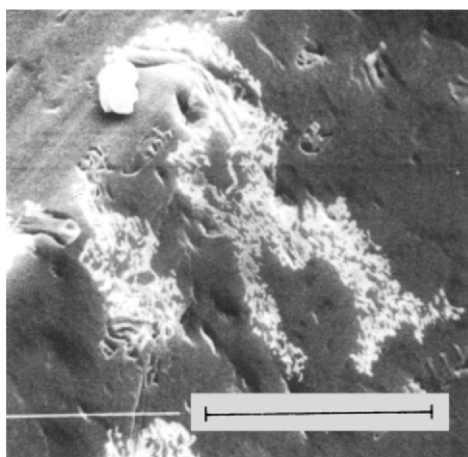


Fig. 13 $T = 390\text{ K}$, $\alpha = 0.01$, carbon dioxide, bar = $10\ \mu\text{m}$

in carbon dioxide produced very different morphology in the product (Fig. 14). The material consisted of porous crystals with outgrowths, the size of which varied with degree of decomposition.

Discussion

Reaction Stoichiometry

The evidence from mass losses can be rationalised in the following scheme: (a) Decomposition of sesquicarbonate to

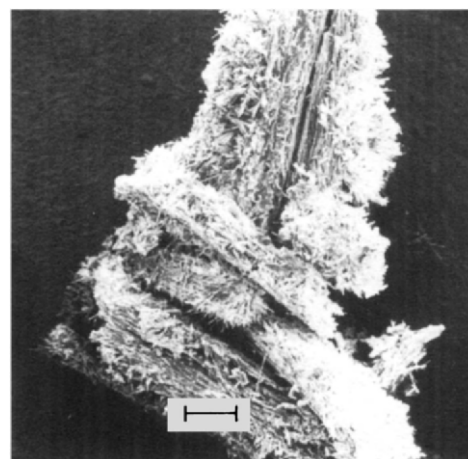
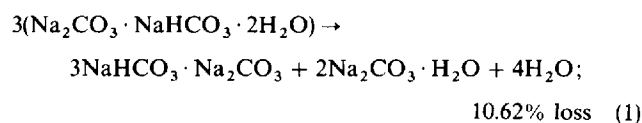
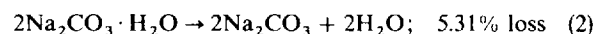


Fig. 14 $T = 390\text{ K}$, $\alpha = 1.0$, carbon dioxide, bar = $110\ \mu\text{m}$

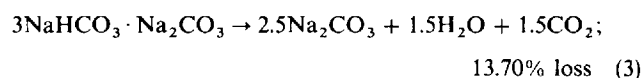
produce wegscheiderite and sodium carbonate monohydrate:



(b) Decomposition of monohydrate:



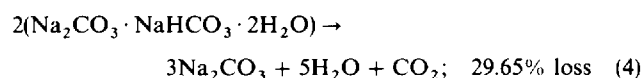
(c) Decomposition of wegscheiderite:



These reactions give rise to the three stages observed in carbon dioxide atmospheres at low temperatures.

Effect of Temperature on Reaction Stoichiometry

At higher temperatures in carbon dioxide, the 5.31% stage disappears, indicating that monohydrate is decomposing while wegscheiderite is stable. Further increase in temperature produces a single-stage reaction, indicating that wegscheiderite is also unstable. The reaction stoichiometry at this stage is as follows:



The identity of the end products was confirmed by X-ray diffraction, as was the presence of monohydrate and wegscheiderite in a sample of sesquicarbonate heated in carbon dioxide at 410 K for 10 min. This scheme differs from that of Gancy³ only in the suggestion that sodium carbonate monohydrate, rather than the anhydrous compound, occurs as an intermediate. Monohydrate is obviously close to the limits of its thermodynamic stability, though under these conditions the decomposition is slow enough to be detected.

Effect of Gas Atmosphere

The two gases used have very different effects on the first three reactions outlined above, and on the stability of the reaction intermediates.

Nitrogen

In the decomposition of sesquicarbonate the partial pressures of both water vapour and carbon dioxide will be kept low by flowing nitrogen [reaction (4)], so driving the equilibrium to

the right. Both monohydrate and wegscheiderite are decomposed as fast as they are formed and the single-stage decomposition is observed.

Carbon Dioxide

In carbon dioxide, two effects are possible: (i) For the decomposition of sesquicarbonate [reaction (1)] and monohydrate [reaction (2)], which have only water as product, carbon dioxide will behave as an inert gas in reducing the partial pressure of water vapour over the solid, thus driving both equilibria to the right.

(ii) For the decomposition of wegscheiderite, however [reaction (3)], carbon dioxide will retard the reaction. Such retardation by carbon dioxide will not affect the dehydration of monohydrate which therefore decomposes before wegscheiderite. This retardation obviously breaks down at ca. 430 K, since at this temperature the overall reaction ceases to be multi-stage and becomes single stage [reaction (4)]. That the high-temperature, single-stage reaction is also retarded in carbon dioxide atmospheres relative to nitrogen, suggests that a reaction involving carbon dioxide, *i.e.* wegscheiderite decomposition, is rate controlling. Thus the observed sequence of reactions can be accounted for. The occurrence of feathery outgrowths visible in micrographs of the product from the single-stage decomposition in nitrogen (Fig. 6), which do not occur in the decomposition in carbon dioxide, suggests that these may be caused by rapid dehydration of monohydrate. It is possible that a saturated solution is formed during this stage and the solution is forced to the surface where the solvent evaporates rapidly, leaving behind the outgrowths.

Kinetics and Mechanisms of Decomposition

In Nitrogen

The decomposition appears to be single stage across the temperature range studied (350–460 K) and the reduced time plots indicate that Avrami–Erofev kinetics, with $n = 2$, are being followed. There is a change of slope in the Arrhenius plot at ca. 390 K without any change in mechanism. It is possible to interpret such kinetics in various ways which might relate directly to the decomposition of sesquicarbonate, and which would be in agreement with the microscopic evidence, but the details of the mechanism *etc.* are very similar to those for the dehydration of monohydrate.¹³ These similarities are listed in Table 2. The suggestion is therefore that the rate-controlling step under these conditions is not the decomposition of the nominal reactant, sesquicarbonate, but rather the dehydration of a secondary product, sodium carbonate monohydrate. The results in Table 2 show that the reaction mechanisms and the inflexion temperatures are in agreement, and there are several reasons for the observed difference in activation energy. The decomposition of mono-

hydrate is dependent on the pressure of the water vapour, the value in Table 2 being the limiting value for the decomposition in dry nitrogen atmospheres. Over the same temperature range as used in the present work, the activation energy for the decomposition of monohydrate was shown to be ca. 60 kJ mol⁻¹, this reduction from the dry nitrogen value being caused by a high internal pressure of water vapour increasing the backward, rehydration, rate.¹³

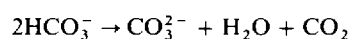
There will be differences caused by variations in crystal size; the size and morphology of the monohydrate crystals produced by reaction (1) along with those of wegscheiderite are not known, but they can reasonably be assumed to be much smaller than those in the sample of pure monohydrate studied previously. For a reaction in which the mechanism is controlled by a nucleation process, the size and perfection of the reacting crystals is likely to be very important.

In Carbon Dioxide

At temperatures above 435 K the single-stage decomposition to sodium carbonate follows contracting disc kinetics with an activation energy of 29 kJ mol⁻¹. The high-temperature thermal decompositions of wegscheiderite and sodium hydrogencarbonate have essentially the same mechanism and Arrhenius parameters.^{11,12} It is reasonable to suggest, therefore, in agreement with the mass losses, that the rate-controlling step for the decomposition of sesquicarbonate at high temperatures in carbon dioxide is the decomposition of wegscheiderite. A comparison of the kinetic data is included in Table 2.

The low-temperature decomposition process in carbon dioxide also has the same mechanism as that of wegscheiderite and hydrogencarbonate,^{11,12} but there is a progressive increase in activation energy from sesquicarbonate, through wegscheiderite to hydrogencarbonate; a comparison of the kinetic data are included in Table 2.

All of these reactions involve essentially the decomposition of pairs of hydrogencarbonate groups:



It is tempting, therefore, to link the increase in activation energy to the complexity of the grouping of hydrogencarbonate ions in the three compounds. Sesquicarbonate has pairs of hydrogen-bonded hydrogencarbonate ions, so that the combination of these should be relatively simple, while in hydrogencarbonate the same ions form infinite hydrogen-bonded chains,¹⁴ in which the correct pairing will be more difficult. Unfortunately, the crystal structure of wegscheiderite has not been determined.

These suggestions help to relate the mechanisms and the activation energies to similar reactions in other compounds, but are apparently contradicted by the low-temperature micrographs, which show the formation of two-dimensional nuclei in both nitrogen and carbon dioxide atmospheres.

Table 2 Comparison of present data on decomposition of sesquicarbonate with published data on wegscheiderite, sodium hydrogencarbonate and monohydrate

	inflexion temperature /K	high-temperature parameters		low-temperature parameters	
		activation energy /kJ mol ⁻¹	reaction mechanism ^a	activation energy /kJ mol ⁻¹	reaction mechanism ^a
this work ^b	390	24	A2	58	A2
monohydrate ^{b,c}	385	20	A2	72	A2
this work ^d	420	29	R2	67	F1
wegscheiderite ^{d,e}	410	28	R3	94	F1
hydrogencarbonate ^{d,f}	415	32	R3	130	F1

^a See Table 1 for an explanation of the symbols. ^b In nitrogen atmosphere. ^c Ref. 13. ^d In carbon dioxide atmosphere. ^e Ref. 11. ^f Ref. 12.

These must relate to the decomposition of sesquicarbonate, but, in the case of nitrogen, not to the rate-controlling step. These nuclei are more difficult to explain in the carbon dioxide case, particularly when associated with the outgrowths at higher conversions. Several interpretations of the first-order kinetics are possible and these have been outlined in previous papers.^{11,12} The decompositions of both sodium hydrogencarbonate and wegscheiderite show product outgrowths, and both follow first-order kinetics. The explanation of first-order kinetics is different in each of these cases, and the present results are very similar to those for the decomposition of wegscheiderite, with the best interpretation being in terms of a constant number of nuclei growing one-dimensionally, but as in that case,¹¹ the micrographs cannot easily be related to the observed first-order kinetics.

Conclusions

The thermal decomposition of sodium sesquicarbonate produces two reaction intermediates, sodium carbonate monohydrate and wegscheiderite. The thermal decomposition of these intermediates is the rate-controlling step across a wide range of temperatures and atmospheric composition.

Only at low temperatures, in carbon dioxide, is the decomposition of sesquicarbonate rate controlling. For this low-temperature decomposition in carbon dioxide, the

microscopic evidence cannot be related directly to the bulk kinetics.

We thank ICI Chemicals and Polymers Group for their generous support of this research programme and Dr. N. Rolfe for his interest.

References

- 1 R. W. Purcell, in *The Modern Inorganic Chemicals Industry*, ed. R. Thompson, The Chemical Society, London, 1977.
- 2 M. H. Lescoeur, *Ann. Chim. Phys.*, 1892, **6**, 423.
- 3 A. B. Gancy, *J. Chem. Eng. Data*, 1963, **8**, 301.
- 4 N. F. Yushkevich and A. V. Avdeeva, *J. Chem. Ind. (Moscow)*, 1931, **8**, 4.
- 5 E. M. Mitkevich, *Zh. Prikl. Khim.*, 1958, **31**, 158.
- 6 D. R. Torgeson, *Ind. Chem. Eng.*, 1948, **40**, 1152.
- 7 C. W. Beck, *Am. Miner.*, 1950, **35**, 98.
- 8 G. E. Bacon and N. A. Curry, *Acta Crystallogr.*, 1956, **9**, 82.
- 9 ASTM Index, Card No. 11-643, JCPDS.
- 10 J. H. Sharp, G. W. Brindley and B. N. N. Achar, *J. Am. Ceram. Soc.*, 1966, **49**, 379.
- 11 M. C. Ball, A. N. Strachan and R. M. Strachan, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1911.
- 12 M. C. Ball, C. M. Snelling, A. N. Strachan and R. M. Strachan, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 3709.
- 13 M. C. Ball, C. M. Snelling and A. N. Strachan, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1761.
- 14 R. W. G. Wyckoff, *Crystal Structures*, Wiley-Interscience, New York, 1964, vol. 2, p. 459.

Paper 1/05260H; Received 16th October, 1991