DRUG DEVELOPMENT COMMUNICATIONS, 1(1), 29-38 (1974-1975)

A KINETIC STUDY OF THE SOLID STATE TRANSFORMATION OF SODIUM BICARBONATE TO SODIUM CARBONATE

Eli Shefter[1], Albert Lo[1], and S. Ramalingam[2]

[1]Department of Pharmaceutics, School of Pharmacy
State University of New York at Buffalo
Buffalo, New York 14214

[2]Department of Mechanical Engineering
State University of New York at Buffalo
Buffalo, New York 14214

ABSTRACT

The thermal transformation of sodium bicarbonate to anhydrous sodium carbonate was studied in an open system between 82°C and 95°C by an x-ray powder diffraction method. The kinetic behavior of this transformation for finely ground material can be ascribed to the "diminishing sphere" model (1/3 order). In the transformation process an intermediate state lacking crystallinity was observed. This state is attributed to the formation of numerous surface nuclei of anhydrous sodium carbonate.

Thermal methods have been employed by a number of investigators (1 and 2) to study the decomposition of crystalline sodium bicarbonate. The investigations using thermal gravimetric analysis and differential thermal analysis suggest that the dehydration process for sodium bicarbonate can be quite complex kinetically.

X-ray diffraction methods can be employed in solid state kinetics to monitor the crystalline quantities of the reactants, products, and in certain instances, intermediates. Quantitative data on the physical state of a solid state reaction can be used to compliment chemically and thermally derived information on the system. An x-ray study was initiated on the termally induced decomposition of crystalline sodium bicarbonate, to learn more about the complexity of this reaction. The preliminary findings of this study are here-in reported.

EXPERIMENTAL

Materials: Samples of sodium bicarbonate (Reagent) grade[1]) were sieved for these studies. The fraction which passed through a number 140 sieve and retained on a number 170 sieve was used (sieve openings are 0.105 mm and 0.088 mm, respectively[2]).

[1]J.T. Baker Chemical Co., Phillipsburg, New Jersey

[2]Newark Instruments, Inc., Fullerton, California

Procedure: The procedure used is similar to that outlined in a previous paper (3). A sample is heated at a particular temperature in a specially constructed x-ray powder holder. The x-ray diffraction pattern in certain two theta (2θ) and the appearance of a peak at 38.2° (2θ) due to the presence of anhydrous crystalline sodium carbonate were measured. These two peak were choosen for the analysis as they do not overlap with any peaks in the diffraction pattern of the other, and they are of sufficient intensity for quantitative anlysis. Samples prepared with known amounts of crystalline sodium bicarbonate and sodium carbonate (both reagent grade) showed that a linear relationship exists between their fractional amount and the intensity (the intensity being taken as half the peak height times the peak width at the base line) of the respective diffraction maxima.

A Toshiba ADG-301 Diffpet x-ray diffractometer[3] equipped with a geiger-müller detector was used for the measurements. The radiation used was Nickel filtered Cu Kα.

Studies were carried out between 82°C and 95°C (temperatures on the bottom surface of the powder bed). As pointed out in an earlier report (3), the surface

---

[3]Beckman Instruments, Inc., Fullerton, California

particles, those in contact with the atmosphere, are approximately 10°C lower in temperature. The amount of moisture and carbon dioxide in the atmosphere above the samples was not controlled in these experiments (open system at room conditions).

RESULTS AND DISCUSSION

Anhydrous sodium carbonate appeared to be the only crystalline material formed under the conditions of the experiments. There was no indication of any crystalline hydrates or complex salts in the measured x-ray diffraction patterns.

The fractional amounts of bicarbonate and carbonate in a sample maintained at 93°C are shown in Figure 1. The shapes of the curves have similar appearances at each of the temperatures studied; only gradients differ significantly. The total quantity of crystalline material (estimated as a sum of the fractional amounts of crystalline carbonate and bicarbonate) was less than 100 percent after the reaction is initiated. The deterioration of the sample crystallinity reaches a minimum and then continues to improve. After all the bicarbonate is depleted the crystalline anhydrous sodium carbonate continues to appear.

The sodium bicarbonate diffraction maxima were found to exhibit significant line broadening. The extent of the broadening of the peaks suggests that

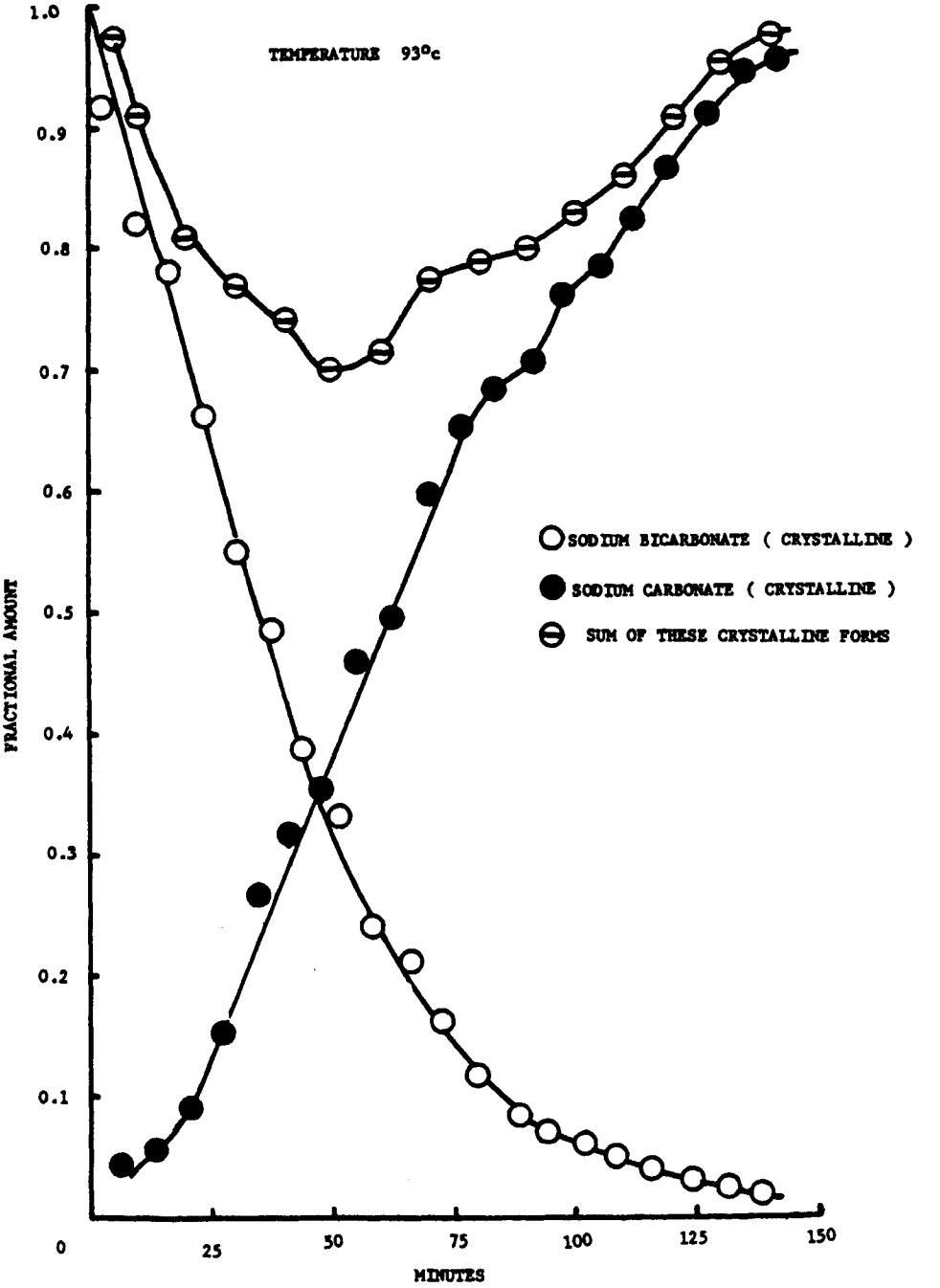

FIGURE 1.

numerous small crystallites of carbonate were forming. This in turn is a good indication that the intermediate noncrystalline phase (non-diffracting) is actually small nuclei of anhydrous sodium carbonate. Particles which are less than 10^{-6} cm in size would not be expected to give rise to typical x-ray powder patterns, but to a diffuse continuous background (4).

The rate of bicarbonate disappearance seems to proceed via surface controlled kinetics. This is seen in the adherence of the data to cube root kinetics (diminishing sphere model) (5). Figure 2 shows the cube root of the fraction of bicarbonate remaining plotted against time for two temperatures. The biphasic character of these plots was found throughout the temperature range studied. The reason for two unique slopes in these plots has not been delineated. One possibility is that the gaseous products (CO_2 + H_2O) may influence the mechanism by surface adsorption, and another possibility is that thermal diffusion in the sample due to the experimental set-up creates such an effect. In any case Arrhenius plots of the initial slope (k_1) and the secondary slope (k_2) were linear (see Figure 3). The activation energies associated with these kinetic parameters are given in the Figure.

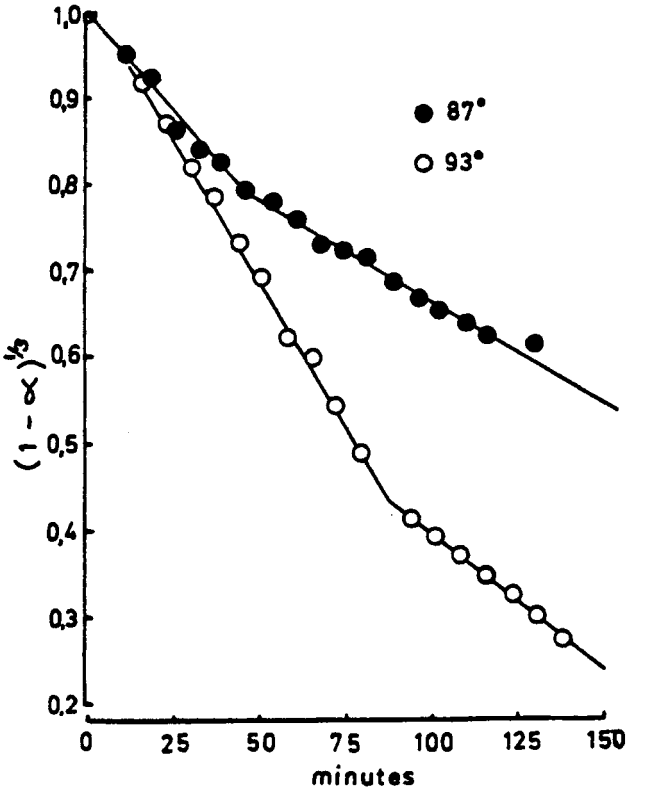

FIGURE 2.

Dehydration of sodium bicarbonate plotted by the cube root law.

these crystals are heated for a short period, such that only about 5% is converted to carbonate, the surface appearance changes dramatically. Numerous very fine lath-shaped crystals of anhydrous sodium

[4]JOEL (USA) Inc., Medford, Mass.

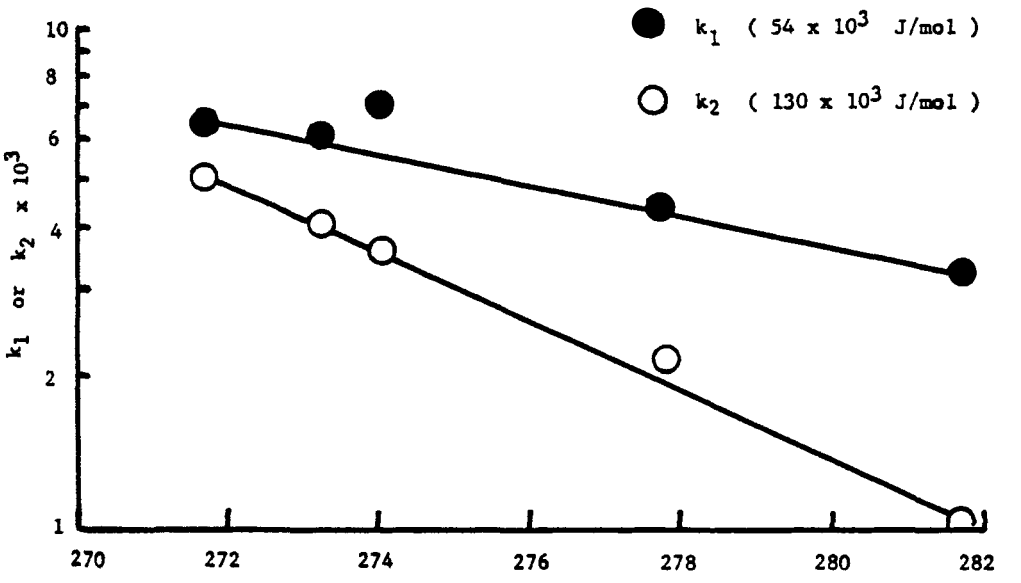

FIGURE 3.

Arrhenius plot.

carbonate appear on the surface. This indicates that the decomposition is indeed surface controlled, and that the non-crystalline intermediate is most likely nuclei of anhydrous sodium carbonate.

Scanning electron micrographs (a JSM-U3 SEM was used[4]) of sodium bicarbonate crystals which were heated for a short period gave further insight into the mechansim. The surface of freshly crystallized bicarbonate is shown in the Figure 4a. When

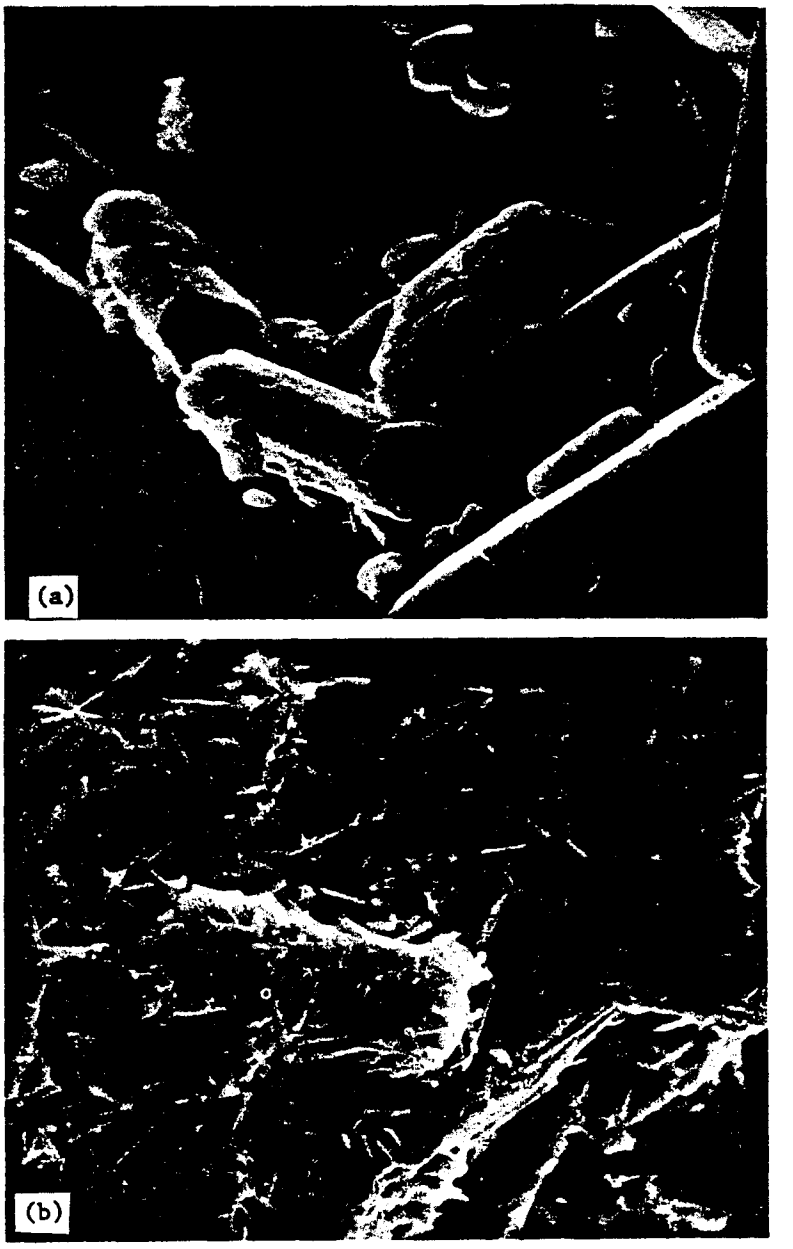

FIGURE 4.
Scanning electron micrographs of sodium bicarbonate crystals before (a) and after (b) heat treatment for a short period. Original magnification 1000 X, present magnification 900 X.

In conclusion, one could make use of such surface controlled phenomena in dosage from design. Anhydrous materials in the presence of small amounts of moisture are in many instances easier to compress into tablets. Thus slight heat treatment of hydrates or solvates can cover their surface with a sufficient number of anhydrous crystals to facilitate their compression into tablets. Dissolution characteristics of pharmaceuticals could be altered by varying the surface depth of the anhydrous species.

REFERENCES

1. E.M. Barrall and L.B. Rogers, J. Inorg. Nucl. Chem. 28, 41 (1966).
2. R. Tsuchiya, J. Chem. Soc. Japan, Pure Chem. Sec. 74, 12 (1953.
3. E. Shefter, H.L. Fung, O. Mok, J. Pharm. Sci. 00, 0000 (1973).
4. L.V. Azaroff and M.J. Buerger, The Powder Method, McGraw-Hill Book Co., New York, 1958, p. 255.
5. P.W.M. Jacobs and F.C. Tompkins, in Chemistry of the Solid State, W.E. Garner, Ed. Butterworth Scientific Publications, London, England, 1955, p. 201.