

Notes

THERMAL DECOMPOSITION KINETICS OF SODIUM BICARBONATE BY DIFFERENTIAL THERMAL ANALYSIS

K. S. SUBRAMANIAN, T. P. RADHAKRISHNAN and A. K. SUNDARAM

Analytical Division, Bhabha Atomic Research Centre, Trombay, Bombay, India

(Received October 19, 1970; in revised form June 23, 1971)

The thermal decomposition of sodium bicarbonate has been studied by DTA. It has been shown that the application of the first order kinetic equation provides a convenient quantitative description of the DTA curves. The influence of particle size, dilution, rate of heating and the size of the sample holder has been examined.

Differential thermal analysis (DTA) has become an important tool for the qualitative characterisation of solid phase thermal reactions. In recent years, a quantitative approach of analysing the DTA curve in terms of the kinetic parameters has been proposed [1-4]. In the course of our study on the thermal decomposition of sodium bicarbonate it was observed that the results could be described conveniently by the application of the laws of chemical kinetics. The effect of a number of parameters, viz., rate of heating, particle size, etc., on the DTA curve has been studied.

Experimental

The DTA apparatus comprised a vertical furnace and calibrated [5] chromel-alumel (22 gauge) thermocouples. Programmed heating of the furnace was ensured by a Hartman and Braun (Standard Model 98121) program controller. A Honeywell Brown Elektronik temperature recorder and a Bausch and Lomb VOM-7 recorder were used to record the sample or reference temperature and the differential temperature, respectively.

Sodium bicarbonate (B.D.H., AnalaR) was obtained in the desired ranges of particle size by sieving: 50-100 mesh (300 μ), 100-200 mesh (96 μ), 200-325 mesh (56 μ) and >325 mesh (14 μ). Alumina (E. Merck, chromatographic grade) was used both as the diluent and reference material.

Two different sample holders made of 20 gauge platinum were used. Sodium bicarbonate was packed in the sample holder between two layers of alumina (large sample holder: 160-180 mg Al_2O_3 and 60-80 mg of sample, small holder: 60-80 mg and 25-50 mg, respectively).

Results and discussion

Several authors have derived expressions for the evaluation of the kinetic parameters for thermal decomposition reactions using a lumped parameter model of the heat transfer process and with the implicit assumption that the Arrhenius rate equation is applicable. Borchardt and Daniels [1] limited their study to stirred solutions. Several workers [6–8] have, however, applied this method for solid state decomposition reactions and the results are in good agreement with those

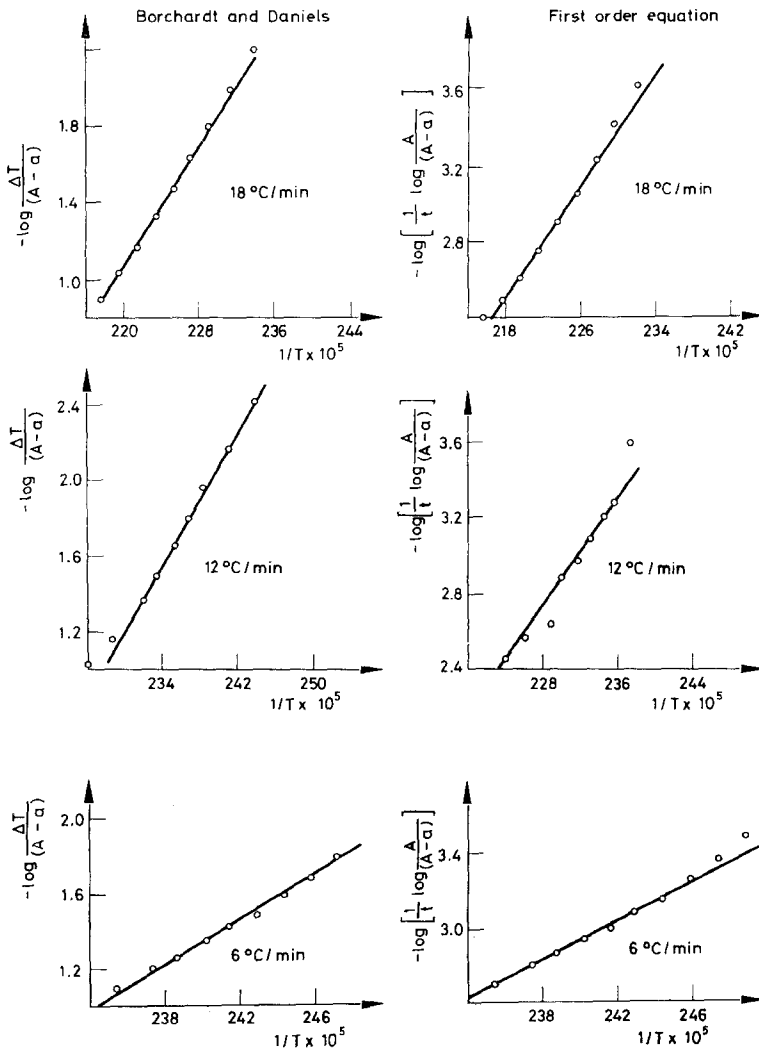


Fig. 1. Thermal decomposition kinetics of sodium bicarbonate by differential thermal analysis

obtained by thermogravimetry. Reed et al. [9] and recently, Melling et al. [10] have made a detailed mathematical study of DTA curves and have pointed out that the fundamental assumptions of Borchardt and Daniels are valid only for stirred solutions where there is no temperature gradient within the sample. With this limitation in mind the simplified expression of Borchardt and Daniels has been used in the present study for purposes of comparison. The DTA curves for the decomposition of sodium bicarbonate have been investigated by the application of the first order kinetic equation. The influence of rate of heating, particle size, size of sample holder, etc., has also been studied.

The equation for the first order reaction is given by

$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x} \quad (1)$$

where a_0 is the initial amount of the substance and x is the amount decomposed at time, t . In DTA, a_0 corresponds to the total area, A and x correspond to the area, a , swept at time, t . Hence, Eq. (1) can be written as

$$k = \frac{1}{t} \ln \frac{A}{A - a} \quad (2)$$

The rate constant was calculated at different temperatures from the DTA curve. The reaction obeyed the Arrhenius law for a first order reaction as could be seen from a plot of $\log \left[\frac{1}{t} \log \frac{A}{A - a} \right]$ vs. $\frac{1}{T}$ (Fig. 1). The energies of activation calculated at different heating rates were in agreement (Table 1) with those obtained by the use of the simplified expression of Borchardt and Daniels $\left(\log \frac{\Delta T}{A - a} \text{ vs. } \frac{1}{T} \right)$.

Table 1
Effect of particle size and heating rate

Heating rate, °C/min	Method	Particle size (mesh)			
		50-100	100-200	200-325	> 325
<i>E</i> kcal/mole					
6	a	23	24	23	22
	b	21	24	22	21
12	a	22	22	23	23
	b	21	22	23	22
18	a	20	21	19	20
	b	21	20	21	20

a - Method of Borchardt and Daniels.

b - Present method: First order kinetic equation.

Effect of other parameters

Earlier work on the influence of particle size [11–13] on the slope and position of the DTA peak was concerned mainly with minerals and not much work was carried out with inorganic and organic substances. With minerals, in general, there was only a slight decrease in the peak temperature with particle size. The peak temperature for the decomposition of calcium carbonate was not affected [14] by particle sizes in the range of 26 to 1 μ . Rose and English [15] showed further that the mean particle size had no effect on the size, shape and position of the peak.

The decomposition of sodium bicarbonate was studied at different particle sizes and at different heating rates. It was observed (Table 1) that particle size in the range of 10–300 μ and heating rate of 6–18°/min had no effect on the kinetics of the reaction. The results were also not altered by diluting the sample or by the use of sample holders of different dimensions (Table 2).

Table 2
Effect of sample holder dimensions and dilution

Heating rate, °C/min	Method	E, kcal/mole			
		50–100 mesh		100–200 mesh	
		Undiluted	Diluted ^c	Large holder	Small holder
6	a	22	23	—	—
	b	20	21	—	—
12	a	21	22	22	22
	b	19	21	21	21
18	a	22	20	—	—
	b	21	21	—	—

a — Method of Borchardt and Daniels

b — Present method: First-order kinetic equation

c — Sample diluted in the ratio 1 : 4

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The authors wish to thank Shri G. V. U. Rao, Metallurgy Division, B.A.R.C., for the microscopic determination of the particle size of sodium bicarbonate samples.

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