A THERMOGRAVIMETRIC STUDY OF THE DECOMPOSITION OF SODIUM BICARBONATE

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Abstract

A thermogravimetric study of the decomposition of sodium bicarbonate has been carried out. The energy of activation of 20 ± 2 kcal/mole calculated by the methods of Coats and Redfern as well as Freeman and Carroll is found to be independent of the rate of heating and particle size.

Introduction

Thermogravimetry has become a versatile technique for the study of the kinetics of the thermal decomposition of hydrates, carbonates, oxalates, etc., and several methods[1–9] have been proposed for the evaluation of the energy of activation of the reaction. This paper describes a study of the decomposition of sodium bicarbonate and the energy of activation has been calculated by the methods of Freeman and Carroll as well as Coats and Redfern. The effects of heating rate and particle size, in particular, on the activation energy have been studied.

Experimental

The thermogravimetric apparatus was set up using a Cahn RG-Electrobalance (M/s. Cahn Instrument Co., U.S.A). A Bausch and Lomb VOM 7 strip chart recorder (1mV scale) was used for recording the weight-loss, at a sensitivity corresponding to 0·1 mg./div. The recorded weight-loss, was accurate to within ± 0·5% of the theoretical values. Programmed heating of the furnace at 2, 4 or 6° C./min. was achieved with a Mahindra 'Electroflo' on-off programme controller. The power input to the furnace was regulated through a manually operated variac and the rate of heating was reproducible to better than ± 0·5° C./min. A thin platinum foil was used as the sample pan. Accurate measurement of sample temperature was ensured by placing

a chromel-alumel thermocouple (22 gauge) close to and within 5 mm. of the bottom of the sample pan and the temperature was read from a Honeywell Brown Elecktronik Temperature Recorder. The weight of the sample varied from 13 to 24 mg. All experiments were carried out in static air with open sample holders.

Sodium bicarbonate (B.D.H., AnalaR) was powdered and sieved to get particle sizes in different ranges. The mesh size and the corresponding average particle sizes determined microscopically were as follows: 50–100 mesh (300 μ), 100–200 mesh (96 μ), 200–325 mesh (56 μ) and $>$ 325 mesh (14 μ).

Results and Discussion

Typical thermograms for sodium bicarbonate obtained at different heating rates and particle sizes are given in Fig. 1. Although a number of methods have been suggested for the evaluation of the kinetic parameters

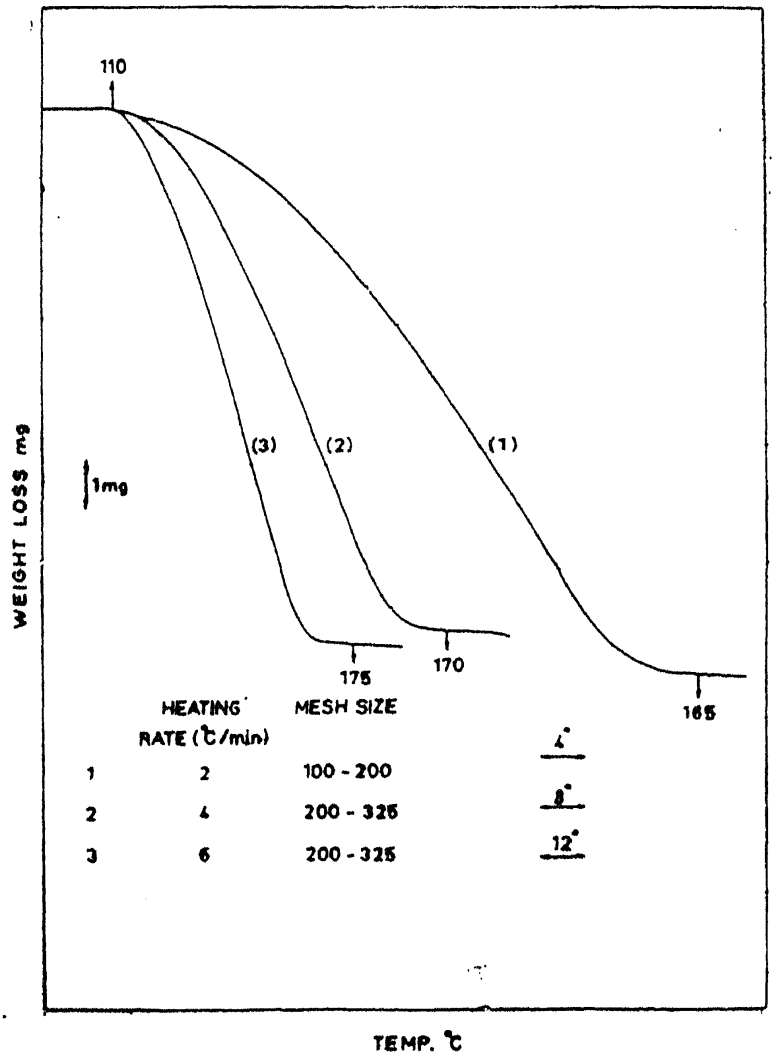

Fig. 1. Typical thermograms.

of solid state reactions from thermograms, the methods of Coats and Redfern[2] and Freeman and Carroll[1] have been used for calculating the energy of activation. The former method provides simplicity and accuracy while the latter serves as well to determine the order of reaction.

According to Coats and Redfern, a first order decomposition reaction can be represented by

$$-\log\left[\frac{2\cdot303}{T^2}\log(1-\alpha)^{-1}\right]=\frac{AR}{aE}\left[1-\frac{2RT}{E}-\frac{E}{2\cdot303\,RT}\right] \quad (1)$$

where α is the fraction decomposed at temperature T, A is the frequency factor, a is the rate of heating and E is the energy of activation. A plot of the left-hand side of eq. 1 *vs.* 1/T should give a straight line with the slope equal to $-E/2\cdot303\ R$. Freeman and Carroll obtained the expression

$$\frac{-\frac{E}{2\cdot303R}\triangle\left(\frac{1}{T}\right)}{\triangle\log W_r}=-n+\frac{\triangle\log\frac{dW}{dt}}{\triangle\log W_r} \quad (2)$$

where W_r is the difference between the total and final weight loss at any temperature, from which the activation energy and the order of reaction, n, can be obtained.

Eqs. 1 and 2 were applied to the study of the decomposition of sodium bicarbonate and from the slope of the plots (Fig. 2), the energy of activation was calculated (Table I) as 20 ± 2 Kcal/mole. This was in agreement with the reported values [10,11] and also with that obtained in our earlier studies by DTA.[12] Leo Reich,[13] however, obtained a value of 24 kcal/mole.

Effect of Particle Size and Heating Rate

The activation energy for the decomposition of sodium bicarbonate was independent of both the particle size and rate of heating (Table I) in conformity with our results obtained by DTA for heating rates of 6–8°C./min. (*loc. cit.*). The activation energy for the dehydration of calcium oxalate monohydrate was, however, found by other workers[14] to be influenced by heating rate and particle size of the sample and was independent of the rate of heating only in the range of 300–325 mesh. Others [15–17] further concluded that the apparent dependence of the value on these two parameters was due to the inherent limitations in the methods used for evaluating the activation energy. Our results are in agreement with the view of Sestack[18] that the activation energy is independent of particle size and rate of heating.

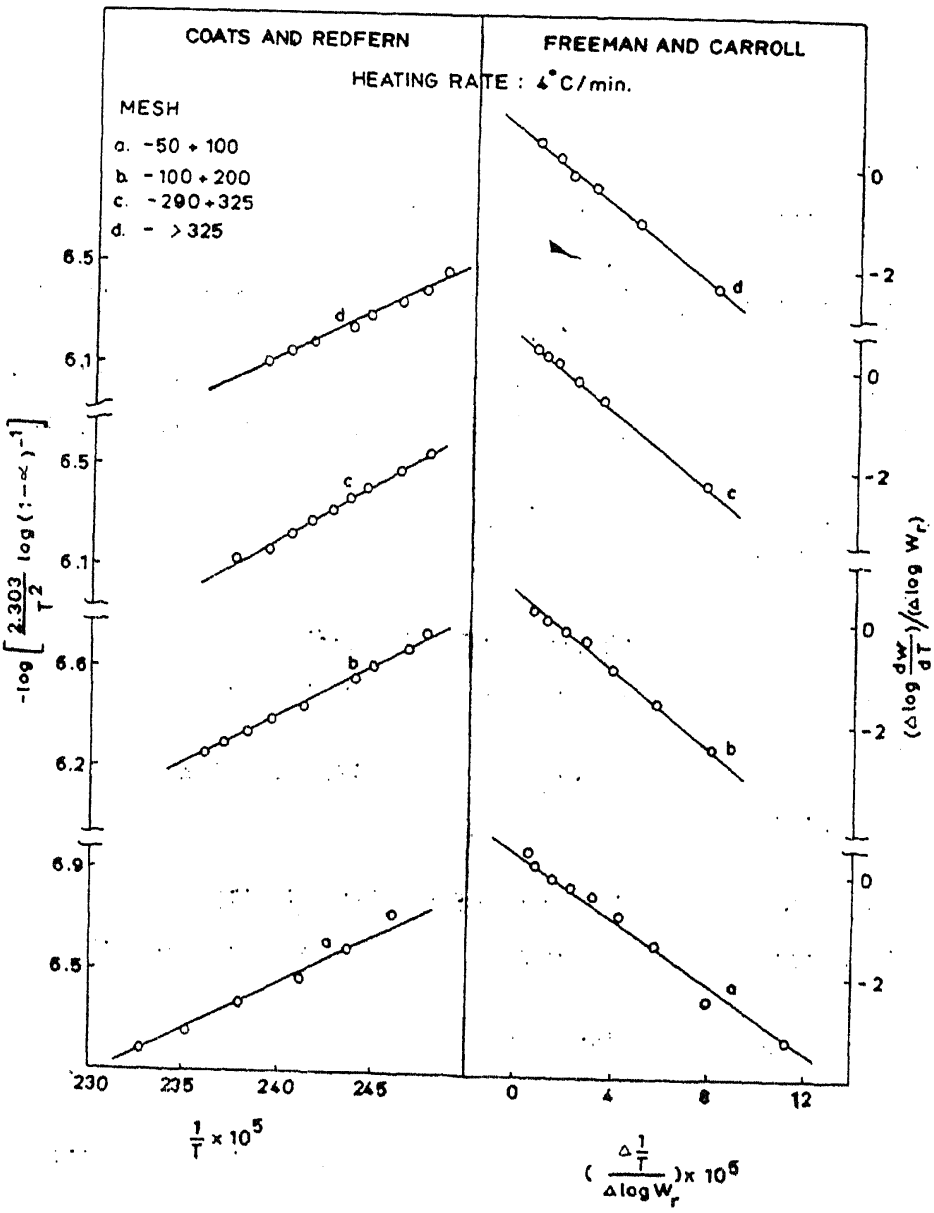

FIG. 2. Activation energy plots.

TABLE I

Values of Activation Energy

Heating rate °C./min.	E Kcal/mole mesh size							
	50–100		100–200		200–325		>325	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
2	20	19	19	21	20	22	21	22
4	18	19	19	20	19	20	19	20
6	19	20	19	20	19	20	20	20

a,—Method of Freeman and Carroll.

b,—Method of Coats and Redfern.

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