

SIGNIFICANCE OF THE KINETICS OF THERMAL DECOMPOSITION OF NaHCO₃ EVALUATED BY THERMAL ANALYSIS

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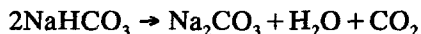
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The Arrhenius parameters and kinetic obedience were determined by TG at constant temperatures as well as at linearly increasing temperatures for the thermal decomposition of sodium hydrogencarbonate. Effects of the sample size (0.5–10 mg) and the particle size on the rate behavior were examined. With such a sample size smaller than ca. 5 mg, an effect of the heating rate was not so critical as is the case with the larger sample size. The Arrhenius parameters and kinetic obedience determined by use of the Ozawa method were in excellent agreement with those determined isothermally. The activation energy E determined with ca. 1 mg of sample was nearly constant independently of the fractional reaction α . Any change in the Arrhenius parameters with different experimental conditions was discussed in connection with the kinetic compensation effect.

Keywords: compensation effect, experimental conditions, kinetics, NaHCO₃, thermal decomposition

Introduction

The thermal decomposition of NaHCO₃ has been the subject of many kinetic studies in the field of theoretical and applied chemistry. This reaction proceeds in a single step to yield Na₂CO₃, which is well known as one of the main stages in the Solvay process.



There are some discrepancies among experimental results reported earlier as well as their interpretation for the kinetics of the decomposition of NaHCO₃ [1–4]. This implies that the kinetics of the reaction is greatly influenced, as is usually the case with solid-state reactions, by the sample and measuring conditions. There should be correspondence, however, about the

interpretation of the kinetic results obtained under the different experimental conditions.

The present work was undertaken to resolve previous perceived inconsistencies and to increase understanding of the reaction by thermogravimetries at constant temperatures and linearly increasing temperatures. It is stressed in particular that thermogravimetric measurements with smaller sample sizes and at lower heating rates are integral to obtain with greater precision the characteristic and reliable rate behavior.

Experimental

Reagent grade of sodium hydrogencarbonate (Katayama Chemical Co., Japan) was ground lightly with a mortar and pestle, and sieved to -48 , $-170+200$, $-350+400$ mesh fractions. 0.5–10 mg of the sample were loaded onto a platinum pan of 5 mm diameter and 2.5 mm height in a Shimadzu TGA-50 system. Isothermal mass loss due to the thermal decomposition of NaHCO_3 was recorded at various constant temperatures in N_2 flowing at a rate of 30 ml/min. Thermogravimetric (TG) curves of the non-isothermal decomposition were obtained at different heating rates. The data were processed by a microcomputer with a plotter.

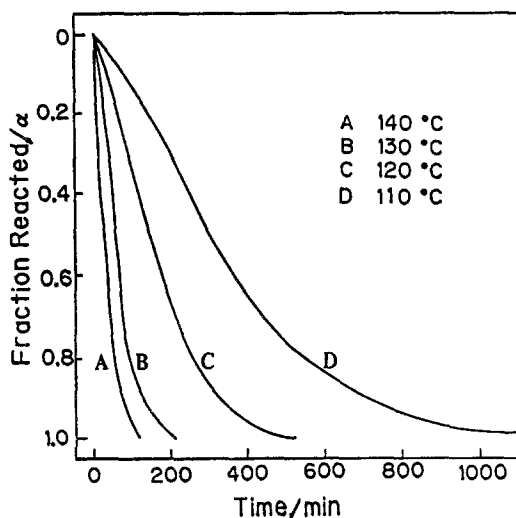


Fig. 1 Typical mass loss curves for the isothermal decomposition of NaHCO_3 . The sample size, 1.0 mg; the particle size fraction, -48 mesh

Results and discussion

Analysis with a sample size of 1.0 mg. Figure 1 shows typical isothermal mass loss changes for the decomposition of 1.0 mg of NaHCO_3 at various temperatures. Table 1 shows the kinetic obedience for the isothermal decomposition determined from the conventional plots of $F(\alpha)$ vs. t [5], together with the activation energy E and the preexponential factor A determined from the Arrhenius plot.

Table 1 The kinetic obedience and the Arrhenius parameters determined for the isothermal decomposition of NaHCO_3

Particle size / mesh	$F(\alpha)^{*1}$	$E / \text{kJ mol}^{-1}$	$\log A / \text{s}^{-1}$	$-\gamma^{*2}$
-48	$R_{2.4}$	102 ± 3	9.08 ± 0.34	0.9949
	$A_{1.6}$	102 ± 3	9.48 ± 0.34	0.9949
-170 + 200	D_2	96.8 ± 3.7	8.86 ± 0.49	0.9879
	$A_{1.2}$	96.9 ± 3.7	9.33 ± 0.48	0.9883
-350 + 400	D_2	103 ± 1	9.9 ± 0.1	0.9994
	$A_{1.2}$	103 ± 1	10.3 ± 0.1	0.9994

*¹ $R_n = 1 - (1 - \alpha)^{1/n}$, $A_m = [\ln(1 - \alpha)]^{1/m}$, $D_2 = \alpha + (1 - \alpha) \ln(1 - \alpha)$

*² Correlation coefficient for linear regression analysis of the Arrhenius plot.

Figure 2 shows typical TG curves obtained for the thermal decomposition of NaHCO_3 at different heating rates. Table 2 shows the Arrhenius

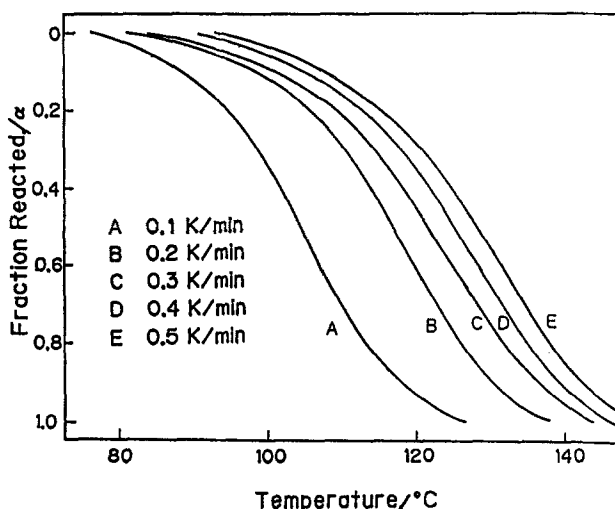


Fig. 2 Typical TG curves for the nonisothermal decomposition of NaHCO_3 . The sample size, 1.0 mg; the particle size fraction, -48 mesh

parameters obtained from the extended Coats and Redfern's method [6, 7] in terms of $F(\alpha)$ determined isothermally, together with the kinetic parameters determined by use of the Ozawa method [8–10].

We see from Tables 1 and 2 that the Arrhenius parameters determined from the three methods are comparable. These results are also comparable with that reported earlier [3].

Table 2 The kinetic parameters obtained for the nonisothermal decomposition of NaHCO_3

Particle size / mesh	The CR method* ¹			The Ozawa method* ³		
	$F(\alpha)$ * ²	$E / \text{kJ mol}^{-1}$	$\log A / \text{s}^{-1}$	$F(\alpha)$ * ⁴	$E / \text{kJ mol}^{-1}$	$\log A / \text{s}^{-1}$
-48	$R_{2.4}$	170	18.2	$R_{2.3}$	98.5	8.6
	$A_{1.6}$	120	11.9	$A_{1.6}$	98.5	9.0
-170 + 200	D_2	207	24.2	$R_{3.0}$	85.1	7.1
	$A_{1.2}$	109	11.1	$A_{1.5}$	85.1	7.6
-350 + 400	D_2	202	23.9	$R_{4.0}$	89.4	7.8
	$A_{1.3}$	101	10.2	$A_{1.3}$	89.4	8.5

*¹ For the decomposition at a heating rate of 0.1 deg/min.

*² The model function determined isothermally.

*³ Analyzed for the decomposition in a heating rate range of 0.1–0.5 deg/min.

*⁴ Determined from the $F(\alpha)$ vs. θ plot (Ref. 10).

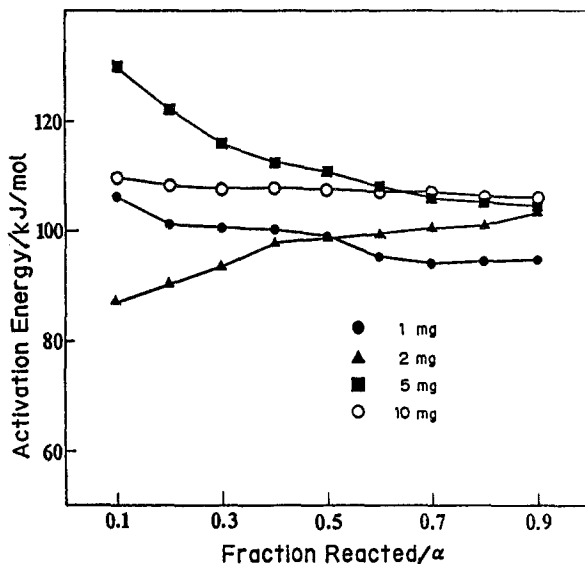


Fig. 3 The effect of the sample size and the fractional reaction α on the activation energy E determined by use of the Ozawa method

Figure 3 shows the dependence of α on the activation energy E determined by use of the Ozawa method. It is noted that E is nearly constant irrespective of α . This result is a marked contrast with that of the thermal dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ with 15 mg of sample [10].

Effect of the sample size on the kinetics of thermal decomposition of NaHCO_3 . Table 3 shows the Arrhenius parameters obtained from the CR method for the nonisothermal decomposition with different sample sizes at various heating rates.

Table 3 Effect of the sample size and heating rate on the Arrhenius parameters obtained from the CR method*

Heating rate / deg min ⁻¹	Sample size / mg					
	1		5		10	
	$E/\text{kJ mol}^{-1}$	$\log A / \text{s}^{-1}$	$E/\text{kJ mol}^{-1}$	$\log A / \text{s}^{-1}$	$E/\text{kJ mol}^{-1}$	$\log A / \text{s}^{-1}$
0.1	120	11.9	102	9.43	88.6	7.63
0.5	89.0	7.84	88.0	7.65	84.6	7.23
1	91.2	8.15	93.6	8.50	82.6	7.01
5	90.5	8.12	86.5	7.65	75.8	6.28
10	84.8	7.49	80.2	6.94	68.0	5.39

* Analyzed for the decomposition of a -48 mesh particle size fraction assuming the kinetic law $A_{1.6}$ determined isothermally with 1.0 mg of sample.

The Arrhenius parameters tend to decrease with the increasing heating rate and sample size. Although this trend is explained by the so-called kinetic compensation effect [11], it is evident that the parameters obtained at a lower heating rate and with a smaller sample size are more reliable and meaningful in view of the experimental condition close to the assumption made in calculating the Arrhenius parameters. As far as the present reaction is concerned, the desirable heating rate and sample size for obtaining reliable Arrhenius parameters are lower than 3 deg/min and smaller than 5 mg, respectively.

It is interesting to note that, as a whole, the E values are roughly constant independent of the sample size and the fractional reaction α (Fig. 3). This fact is different from those obtained for the other system [10]. Such a difference is explained by the kinetic compensation effect, which depends largely on the working temperature interval ΔT [12]. Any change in ΔT implies variation in the kinetics characteristic to a given reaction and/or deviation of the reaction condition from the ideal.

Comparison of the results with those of other workers. It seems meaningful to compare the present results with those obtained under the condition comparable with the present one, in particular with a smaller sample size. The values of E obtained compare with those reported by Van Dooren and Mueller [13] and Hu *et al.* [1].

As for the kinetic obedience, the first order (F_1) law was observed by Hu *et al.* [1]. This is not necessarily contradictory to the present result because the F_1 law was not markedly inferior and the exponent m in the A_m function was extended to nonintegral values between unit and four to find the better linearity [10]. Although it is difficult to rationalize such a nonintegral exponent of m , the A_m law with $m = 1-1.6$ apparently is followed when the true reaction is phase-boundary controlled but there is some distribution of α among particles in the sample bed [2]. The R_n laws with $n = 2.3-3.0$ were obeyed in the present reaction (Tables 1 and 2) and the R_3 law was followed depending on the experimental condition [14].

In conclusion, the kinetic obedience for the thermal decomposition is followed by the R_n law with $n = 2-3$ for each particle in the sample pan and this is likely to be described as the A_m law with $m = 1.0-1.6$ for particles in the pan. The activation energy E obtained, about 100 kJ/mol, seems to be reliable and meaningful since it was determined by TG, both isothermal and nonisothermal, with a small sample size at slow heating rates. The different values of E are obtained when the reaction temperature, in particular the working temperature interval ΔT , is different depending on the experimental condition [12, 15].

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Zusammenfassung — Mittels TG wurden sowohl bei konstanter als auch bei linear ansteigender Temperatur die Arrheniusschen Konstanten und das Kinetikgesetz der thermischen Zersetzung von Natriumhydrogencarbonat bestimmt. Dabei wurde der Einfluß der Probengröße (0.5-10mg) und der Partikelgröße auf das Geschwindigkeitsverhalten untersucht. Mit Proben kleiner als etwa 5 mg ist der Einfluß der Aufheizgeschwindigkeit nicht so groß, wie bei größeren Proben. Die ermittelten Arrheniusschen Parameter und das ermittelte Kinetikgesetz, bestimmt mittels der Methode von Ozawa, stehen in ausgezeichneter Übereinstimmung mit den isotherm ermittelten Resultaten. Die Aktivierungsenergie E bei einer Probe mit einer Masse von etwa 1 mg war nahezu konstant, unabhängig vom Reaktionsgrad. Jede Änderung des Arrheniusschen Parameters infolge von veränderten Versuchsbedingungen wurde in Verbindung mit dem kinetischen Kompensationseffekt diskutiert.