

EFFECT OF THERMAL TRANSPORT MECHANISMS ON THE THERMAL DECOMPOSITION OF CaCO_3 *

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ABSTRACT

Isothermal and dynamic techniques were employed to examine the rate of weight loss of CaCO_3 . Thermogravimetric studies were conducted in atmospheres of He, N_2 , Ar, and various percentages of CO_2 in Ar. Three methods for deriving kinetic parameters from thermogravimetric data were used and these results were then compared with data obtained from isothermal investigations done on identical samples. It was found that the higher the thermal conductivity of the atmosphere, the more rapidly the reaction proceeded. Also, as the percentage of CO_2 in Ar increased, the temperature range of the decomposition became higher and narrower, resulting in a higher activation energy.

INTRODUCTION

There is a wealth of information concerning the thermal decomposition of CaCO_3 . However, there are still some uncertainties as to the actual mechanism and which factors are rate controlling. In a solid state endothermic decomposition, the product-reactant interface usually travels from the exterior surface into the sample, provided it receives the necessary heat of reaction. If this rate of heat transfer is slower than the inherent rate of the reaction, then thermal transport may be rate-determining¹. In an earlier study, Gallagher and Johnson² suggested that thermal transport determines the rate of the decomposition after having observed higher values of apparent activation energy with decreasing heating rate or sample size. Decreasing heating rate or sample size would suggest a lower CO_2 partial pressure and thus a lower activation energy if one considers the generally observed trends of increasing activation energy with increasing CO_2 partial pressure¹. However, the apparent activation energies were actually higher as the heating rate and sample size decreased, so it was concluded that the CO_2 partial pressure was not the rate-determining factor.

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When CO_2 is present in the sweep gas, the thermal decomposition of CaCO_3 will occur at higher temperatures than it would if CO_2 was not present in the sweep gas. At these higher temperatures, thermal transport is more effective due to the T^4 dependence involved in the radiation effects. Thus, the temperature range of the decomposition becomes increasingly narrow as the percentage of CO_2 in the sweep gas increases. From an Arrhenius plot of $\log k$ vs. $1/T$, the wide range of k 's and narrow range of temperatures will generate a steep curve and, therefore, a high apparent activation energy.

EXPERIMENTAL PROCEDURE

For the dynamic measurements, a Perkin-Elmer TGS-1 thermobalance was used. The weight and temperature were recorded as functions of time on punched paper tape³. The CaCO_3 was 20–44 μm fraction of reagent grade material from the J. T. Baker Co. Sample sizes were limited to 4 mg and the sample holder was a small cylindrical Pt cup about 3.5 mm in diameter and 1.2 mm deep. The flow-rate of the various atmospheres (Table 1) was $40 \text{ cm}^3 \text{ min}^{-1}$ down the 20 mm diameter furnace tube. The heating rate was always set at 5°C min^{-1} within the temperature range from room temperature to approximately 1000°C .

TABLE 1

ARRHENIUS PARAMETERS FOR THE DECOMPOSITION OF CaCO_3 IN MIXTURES OF CO_2 AND Ar

Values of E^* are in kcal mol^{-1} and A in sec^{-1} .

% CO_2	Temp. $^\circ\text{C}^*$	Isothermal			Freeman & Carroll			Coats & Redfern			Achar, Brindley & Sharp		
		E^*	A	n	E^*	A	n	E^*	A	n	E^*	A	n
0	745	48	10^8	0.5	52	$5 \cdot 10^8$	0.47	51	$3 \cdot 10^8$	0.5	54	10^9	0.5
5	780	227	16^{45}	0.5	164	$5 \cdot 10^{31}$	1.15	171	$1 \cdot 10^{33}$	1–2	145	$5 \cdot 10^{27}$	1
100	906	—	—	—	512	$5 \cdot 10^{34}$	2.03	503	10^{90}	2	489	10^{87}	2

* Temperature at which there has been a cumulated weight loss of 50%.

The isothermal data were collected using a Cahn balance and electronics which have been described by Gallagher and Johnson⁴. The weight and temperature were recorded as functions of time on magnetic tape. The computer analysis of the data has also been described^{4,5}. The same CaCO_3 was used as in the dynamic experiments and the sample size was again limited to 4 mg. The sample holder was a Pt hemispherical basket having a radius of 2.5 mm and was suspended in a 13 mm diameter fused quartz tube. The atmosphere was passed down the tube at a rate of $40 \text{ cm}^3 \text{ min}^{-1}$. A clam shell-furnace at the desired temperature was then closed around the tube and data collection was begun.

RESULTS AND DISCUSSION

It was found that the decomposition occurred most rapidly in the atmosphere having the highest thermal conductivity, which indicates that the rate of the reaction is dependent upon how quickly heat is supplied to the system. The atmospheres used were He, N₂ and Ar; Fig. 1 shows the thermal conductivity-temperature relationships for these gases. In Fig. 2, the rate constant is plotted against temperature for the three gases using the kinetic data obtained. It is shown that for any temperature, the rate is fastest in He, followed by N₂ and then Ar. Thus, the experimental data indicate that the decomposition proceeds most rapidly in the atmosphere having the highest thermal conductivity.

For experiments in various percentages of CO₂, as the percentage of CO₂ in the sweep gas increased, the temperature range of the decomposition became narrower

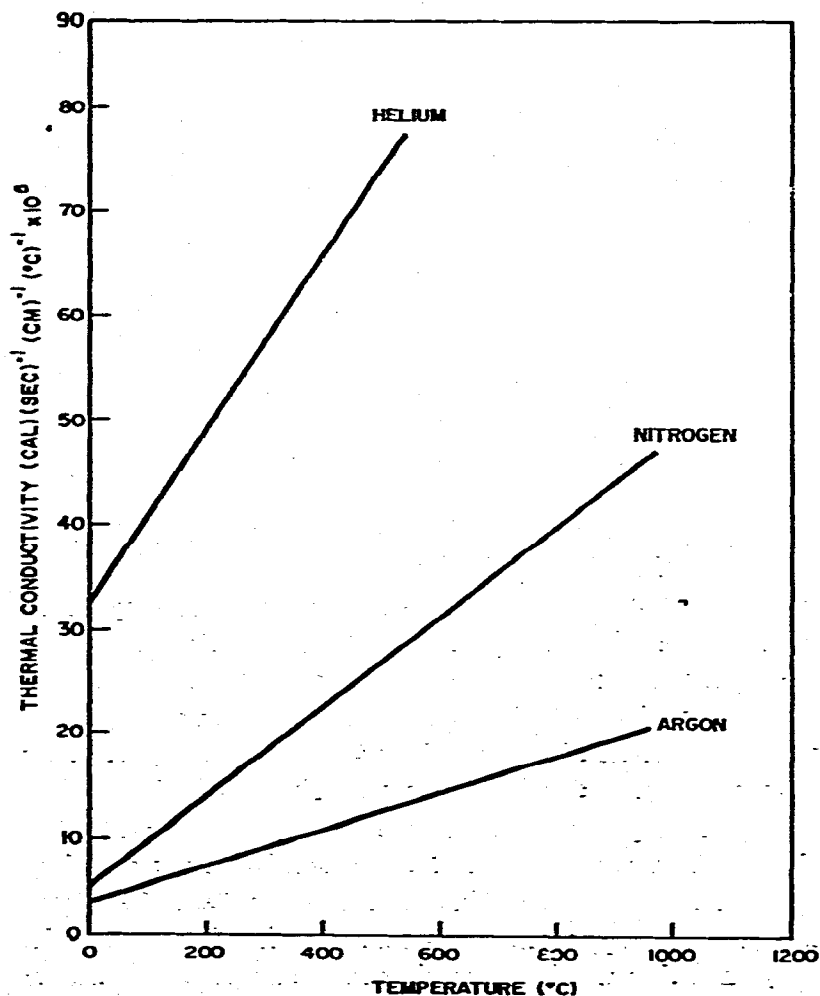


Fig. 1. Thermal conductivity of selected sweep gases.

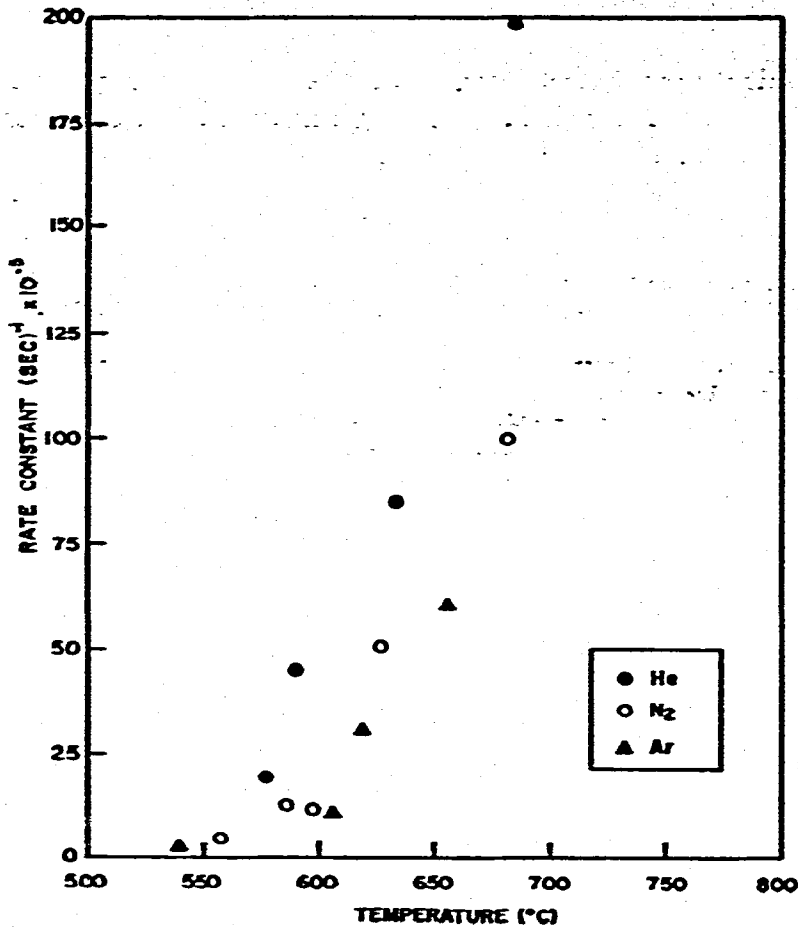


Fig. 2. Rate constants vs. temperature in various sweep gases. $kt = 1 - (1 - \alpha)^{1/2}$.

and shifted to higher temperatures. The range in values of rate constants increased. Thus, the apparent activation energies are higher for a higher CO_2 content (see Table 1) consistent with earlier work². Also, it should be stressed that these apparent activation energies are only indicative of the temperature coefficient of the rate constant and are based upon the temperature of the sensor as opposed to the actual temperature at the reacting interface. From Table 1, one can see that in the dynamic data, the order increases as the CO_2 content increases. This was due to a higher order initial reaction followed by a lower order in the latter stages consistent with isothermal data. That this occurred only when CO_2 was present in the flow gas may suggest that this possible change in mechanism is associated with the reversibility of the reaction. Calculations based upon the Arrhenius parameters in the first line of Table 1 indicate that a rate of 10^{-4} is achieved at an apparent temperature which is about 10°C higher for the dynamic study than for the isothermal study. This is a reasonable temperature lag at this heating rate and is similar to that observed by Gallagher and Johnson² for this heating rate and sample size.

CONCLUSIONS

Thus, we conclude that the rate of the decomposition of CaCO_3 is proportional to the thermal conductivity of the atmosphere, thereby giving support to the theory that the mechanism of this decomposition is thermal transport.

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