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KINETICS OF THE THERMAL DECOMPOSITION OF $CaCO_3$ IN CO_2 AND SOME OBSERVATIONS ON THE KINETIC COMPENSATION EFFECT

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ABSTRACT

The kinetics of the thermal decomposition of $CaCO_3$ in CO_2 were investigated using both dynamic and isothermal techniques. Values of apparent activation energies range from 200–1000 kcal mol^{-1} depending upon sample size and heating rate. It is concluded that thermal transport rather than mass transport or chemical processes is rate determining. The results are compared with earlier work in O_2 and discussed in terms of "the kinetic compensation effect", i.e., the reported linear relationship between the logarithm of the preexponential term and the activation energy derived from the Arrhenius equation.

INTRODUCTION

In earlier work[1] on the kinetics of the decomposition of $CaCO_3$ in a stream of oxygen we had found a very marked dependence upon sample size in isothermal studies and upon both sample size and heating rate in dynamic studies. Correlations were observed between the apparent parameters of the Arrhenius equation, i.e., activation enthalpy (ΔH^*) and the preexponential term (A), with both sample weight and heating rate. We explained the trends toward higher values of apparent ΔH^* with decreasing heating rate or sample size as suggestive that thermal transport controlled the rate of the decomposition.

Recently, Smith et al.[2] have discussed the effects of the partial pressure of CO_2 upon the decomposition of dolomite and have suggested that our results may really have been determined by mass transport of the evolved CO_2 rather than thermal transport. The trend in apparent ΔH^* has been toward higher values with increasing CO_2 partial pressures[3,4]. Since we observed both a decreasing temperature of reaction and increasing values of apparent ΔH^* with decreasing sample sizes and heating rates, this would be contrary to that anticipated based upon high partial pressure of CO_2. However, with increasing sample size and heating rate there is undoubtedly a greater rise in the partial pressure of CO_2 during the course of the decomposition. The mathematical analysis would reflect this as a lower apparent ΔH^*. Therefore, in order to observe these trends as a function of sample size and heating rates without having to contend with the possible change in CO_2 pressure, we have chosen to reinvestigate some of the effects in an atmosphere of pure CO_2.

Correlation of the Arrhenius parameters with the various experimental variables involves consideration of the "kinetic compensation effect". Zsako and Arz[5] have recently described this effect and have fortuitously selected the thermal decomposition of $CaCO_3$ as their example because of the wealth of studies on this compound. Basically this effect is described by the relationship

$$\log A = a\Delta H^* + b \quad (1)$$

where a and b are constants. Essentially this states that observations of a reaction which reveal a higher apparent activation energy are generally compensated by a greater value of the preexponential term. Various ramifications of this will be discussed.

EXPERIMENTAL PROCEDURES

The equipment and data analysis techniques are the same as in our previous study of $CaCO_3$[1]. The same 20–44 μm fraction of J. T. Baker Co. reagent grade material was used. It was dried at 110°C prior to use. Nominally 1, 4, and 16 mg samples were used for the dynamic studies at heating rates of approximately 1.25, 5 and 20°C min^{-1} in a flow of dry CO_2 at 40 cm^3 min^{-1} through a tube of 20 mm i.d. Isothermal studies were performed on nominally 2, 8, and 32 mg samples at 3–4 temperatures in the range of 900–950°C with a flow of dry CO_2 of 40 cm^3 min^{-1} through a tube of 18 mm i.d.

RESULTS AND DISCUSSION

Analysis of the dynamic data indicated that the contracting volume geometry equation, i.e., reaction order, $n = 2/3$, gave the lowest overall standard deviation using either the Achar, Brindley and Sharp[6] (ABS) or the Coats and Redfern[7] (CR) approaches as we use them[1-8]. The actual results are given in Table 1. Results from a Freeman–Carrol[9] analysis are not included because that approach allows n to vary which would cloud the comparisons that we wish to make.

The values of apparent ΔH^* and $\log A$ are very large but consistent with other observers who have worked in pure CO_2[5]. These high values result from the increased steepness of the TG curves despite the higher temperatures at which the reaction occurs. As we reported earlier[1] the trend is towards higher values of apparent ΔH^* and $\log A$ with decreasing sample sizes and heating rates. Since the percentage of CO_2 in the gas phase is invarient during these experiments, the explanation must lie elsewhere. Work is presently underway[10] which indicates that the rate of this reaction in a chemically inert atmosphere is proportional to the thermal conductivity of the atmosphere. This dependence upon thermal conductivity and the trends reported herein and earlier[1] lead us to conclude that the supply of heat is the rate determining factor consistent with the approach of Draper and Sveum[11].

TABLE 1

RESULT OF THE DYNAMIC KINETIC EXPERIMENTS OF THE DECOMPOSITION OF $CaCO_3$ IN CO_2 ASSUMING THE CONTRACTING VOLUME EQUATION

Heating rate (*°C min^{-1}*)	*Method of analysis*	*Nominal sample weight* (*mg*)					
		1		*4*		*16*	
		ΔH^{*a}	*log A*	ΔH^{*a}	*log A*	ΔH^{*a}	*log A*
1.25	ABS	597	101.7	473	80.0	408	69.1
	CR	915	157.7	719	123.3	639	109.8
5.00	ABS	480	80.0	291	47.4	209	33.2
	CR	827	139.9	528	88.3	377	62.3
20.00	ABS	422	71.0	378	63.7	135	21.0
	CR	605	102.6	443	74.5	248	40.6

[a] In kcal mol^{-1}.

In principle, if thermal or mass transport were not important, then the sample interface should begin to decompose when $\Delta G = 0$, and because of the endothermic nature of the reaction, remain at that temperature until decomposed. The temperature at which $\Delta G = 0$ is controlled by the atmosphere for this reversible equilibrium. In one atmosphere of pure CO_2 mass transport becomes negligible and the equilibrium temperature of the reaction, T_R, predicted from thermodynamics is 1160 K (see Fig. 1)[3]. This is considerably higher than the temperatures observed for the decomposition with inert sweep gases. At lower temperatures where thermal transport is slower, isothermal kinetic studies are practical and more informative. However, at

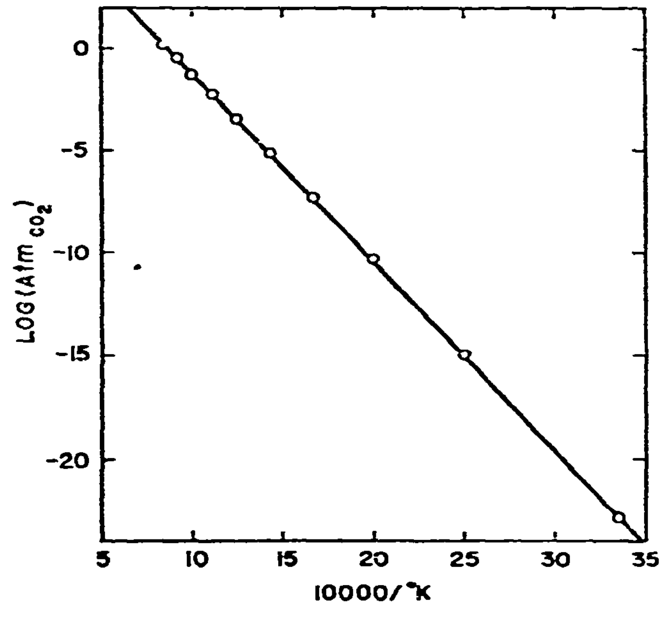

Fig. 1. Equilibrium partial pressure of CO_2 over $CaCO_3$ as a function of temperature[3].

higher temperatures encountered in pure CO_2 where radiative thermal transport becomes dominant due to its T^4 dependence, the rate of thermal energy input is much greater and consequently the rate of the reaction becomes large very quickly. This greatly reduces the accuracy of isothermal techniques because the extent of the reaction during heating to the desired temperature is greater and the range in temperature over which the rate can be satisfactorily measured is much smaller. The latter effect exaggerates the effects of errors in temperature measurement upon the calculated Arrhenius parameters. These conditions, of course, lead to enormous values of apparent ΔH^* and log A similar to the trend observed dynamically.

Because of these difficulties we have chosen not to place great confidence in the isothermal results. Values of apparent ΔH^* varied from 530–693 kcal mol^{-1} and log A from 92.4 to 122.6. These seem reasonable in comparison with Table 1.

Before one makes a detailed analysis of these values of the Arrhenius parameters and compares them with the much lower values observed in our earlier work[1], the relationship between ΔH^* and log A should be considered. Taking the simple form of the Arrhenius equation and merely rearranging yields some insight.

$$k = A\,e^{\frac{-\Delta H^*}{RT}} \tag{2}$$

$$\ln A = \ln K + \frac{1}{RT}\,\Delta H^* \tag{3}$$

A plot of log A vs. ΔH^* should have a slope of $2.303/(RT)$ and an intercept of log K. Garn[12] has also pointed out this rearrangement. The same result can be derived using the expanded form Arrhenius equation in which

$$A = Z\,e^{\frac{\Delta S^*}{R}} \tag{4}$$

where Z is the temperature independent preexponential term, and adapting the common thermodynamic relationships involving changes in heat capacity to activated complex and absolute rate theory

$$\Delta C_p^* = \frac{\mathrm{d}(\Delta H^*)}{\mathrm{d}T} = T\frac{\mathrm{d}(\Delta S^*)}{\mathrm{d}T} \tag{5}$$

yields

$$\frac{\mathrm{d}(\ln A)}{\mathrm{d}(\Delta H^*)} = \frac{1}{RT} \tag{6}$$

The fact that data accumulated over a fairly wide range of temperature would yield such an apparent straight line as indicated in the work of Zsako and Arz[5] indicates that the function within the limits defined by the accuracy of the data is surprisingly insensitive to temperature. Zsako and Arz obtained a slope of 0.195 from a least squares fit of the collected data. This would predict a value of T from eqns (3) or (6) of 1120 K. Considering that the data are collected from experiments without CO_2 additions to the sweep gas all the way to those utilizing pure CO_2, this probably represents a reasonable average temperature. Figure 1 indicates that the equilibrium partial pressure of CO_2 at that temperature is 0.5 atm which is also consistent with this averaging over the range.

Earlier work by Zsako et al.[13], on the decomposition of the complex, $CoBr_2$(*m*-toluidine)$_2$, also exhibited the "kinetic compensation effect" with a much greater slope, 0.475 ± 0.005. This is simply a reflection of the fact that the decomposition takes place at a much lower temperature and, in fact, the value of T (457 K) calculated from the slope is again very near the mid point of the temperature range used in their experimental plots to derive the values of apparent ΔH^* and $\log A$. Garn[12] has also indicated this for the above complexes and for complexes of bis-dioximatocobalt (III) as well as for the reaction of $SrCO_3$ and various samples of TiO_2.

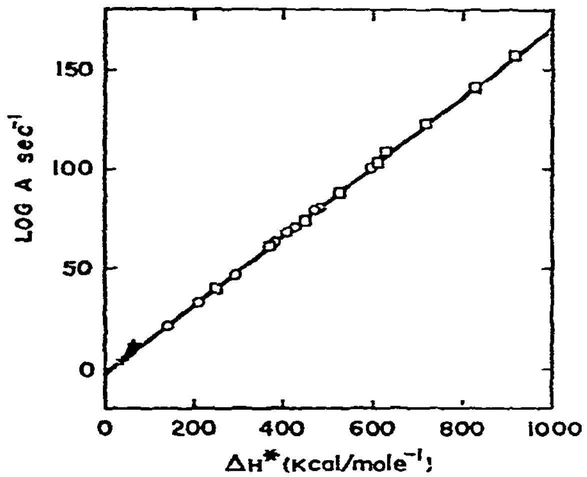

Fig. 2. Kinetic compensation effect for the decomposition of $CaCO_3$ in CO_2. Least squares straight line is $\log A = 0.175\Delta H^* - 2.95$. ○ = Achar, Brindley and Sharp analysis; □ = Coats and Redfern analysis; + = Range from earlier work in O_2.

Our data for CO_2 (Table 1) are plotted in Fig. 2. A reasonably straight line is indicated. A least squares fit yields a slope of 0.175 and an intercept of −2.95. The value of T calculated from this slope is 1243 K, again consistent with the apparent temperature range in which the data were collected. The value of $\log K$ is the rate associated with that of T for any set of ΔH^* and $\log A$ values on the line.

The insensitivity of this plot to temperature can be shown by the short line in Fig. 2 which represents our data from the earlier work[1] in O_2. Figure 3 is an expanded plot of these earlier data and the least squares fit in this instance gives a slope of 0.2778 and an intercept of −5.98. Despite the distinct differences of these values from those derived from Fig. 2, there would be little reason to suspect this from an inspection of

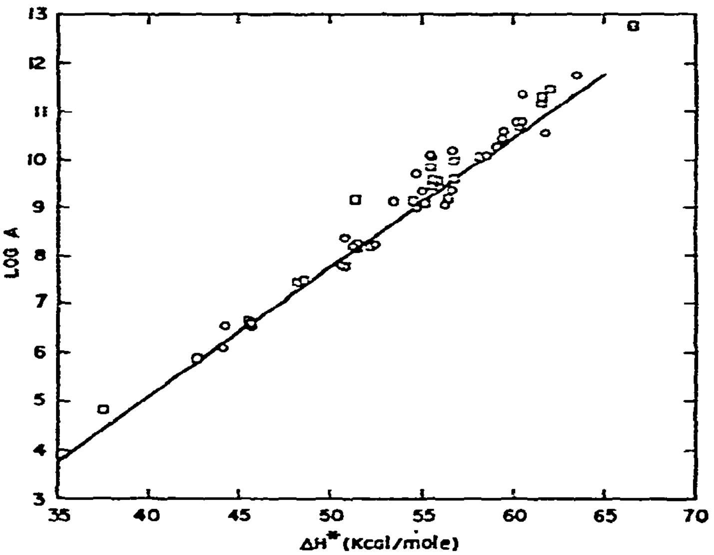

Fig. 3. Kinetic compensation effect for the decomposition of $CaCO_3$ in O_2. Least squares straight line is $\log A = 0.278\Delta H^* - 5.98$. ○ = Achar, Brindley and Sharp analysis; □ = Coats and Redfern analysis.

Fig. 2 or the similar plot in the work of Zsako and Arz[5]. The slope changes smoothly and gradually in such a plot and this change may be readily concealed by the scatter inherent in the data.

These observed changes in the Arrhenius parameters as a function of sample size, heating rate, and temperature regime clearly indicate that the chemical or bond-breaking steps are not rate-determining. We feel further that similar studies on other materials would reveal this to be generally true for thermal decompositions having substantial values of ΔH. That this is not more commonly observed is only due to the fact that many reactions are not reversible or if they are reversible, the pressure of the product is not varied extensively. Consequently the kinetics are seldom determined over a broad temperature range. Wide ranges in sample size and heating rates would also show these effects but require much more effort.

Separating the effects of mass and thermal transport is sometimes difficult. Any set of experimental conditions which will hold the partial pressure of the product gas in the ambient constant will alleviate the problem of mass transport. This is difficult to accomplish experimentally except in an atmosphere of the pure gas. Using an inert sweep gas will tend to keep the concentration of product gas low but it may still vary over several orders of magnitude. Similarly a nearly constant vacuum may be maintained at a gauge by continuous pumping but it is still difficult to maintain a constant pressure of the product gas at the sample interface. Certainly using the smallest sample size and lowest temperatures commensurate with the experimental sensitivity or using self generated or product gas atmospheres are steps in the proper direction.

For a reversible decomposition, e.g., $CaCO_3$, holding the partial pressure of the product gas would establish a temperature of reaction as discussed earlier. This has the effect of increasing the slope of the TG plot and thereby increasing the apparent value of ΔH^*. Changes in apparent ΔH^* are accompanied by the appropriate change in log A as described by the "kinetic compensation effect". Under this condition of constant P_{CO_2} the reaction is then controlled by the ability to supply heat to the reaction interface. Sample packing, holder, and geometry; thermal conductivity of the atmosphere and product layer; and the actual temperature regime of the reaction itself will influence the thermal transport.

Facilitating either thermal transport or mass transport has the same effect of increasing the apparent ΔH^* and log A and decreasing the "measured" temperature of the reaction. It is therefore necessary to study the kinetics under conditions of minimal mass transport effects such as done herein or to systematically correlate the kinetics with thermal transport variables such as is presently under study[10].

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