A Study of the Kinetics of the Basic Zinc Carbonate Formation Reaction

M. F. O'Connor

Institut für Anorganische Chemie der Universität München


Absorption Kinetics, Zinc Oxide, Zinc Hydroxycarbonate

A study of the kinetic parameters involved in the formation of basic zinc carbonate by the action of carbon dioxide and water vapour on zinc oxide has been undertaken. A contracting sphere model is used to explain the reaction but its applicability is dependent upon the carbon dioxide pressure used. Water vapour pressures close to saturated water vapour pressure are necessary for the reaction to proceed and the role of the necessary near-liquid surface water layer in the absorption reaction is discussed.

Introduction

Of the investigations which have so far been conducted concerning the absorption of carbon dioxide by metallic oxides, much is closely related to the thermal decomposition of carbonates and has been studied in order to throw light on this type of reaction\(^1\)\(^-\)\(^4\). The two approaches have much in common and suffer from the same kind of experimental and theoretical disadvantages. For instance, each does not proceed independently of the other; false equilibria can be obtained from either side of equilibrium and the counter-pressure effect in thermal decomposition is analogous to the rate-limiting diffusion of carbon dioxide in the absorption reaction. Studies\(^5\)\(^-\)\(^8\) involving the treatment of zinc oxide surfaces with water vapour and carbon dioxide have shown that water is the preferentially adsorbed species but in these cases no evidence was found of a bulk phase reaction. In a recent publication\(^9\) the interactive roles of water vapour and carbon dioxide in the bulk phase formation of zinc hydroxycarbonate have been discussed and it was found that when the reaction conditions were optimised, zinc oxide could be completely converted to zinc hydroxycarbonate according to the equation

\[
x\text{ZnO} + y\text{CO}_2 + (x-y)\text{H}_2\text{O} = \text{Zn}_x(\text{CO}_3)_{y/2}(\text{OH})_{2(x-y)}
\]

The reaction is explained\(^9\) in terms of the building of an intermediate zinc hydroxide layer which further reacts to form zinc hydroxycarbonate. The strong dependence of the reaction rate on the reaction temperature is more probably due to thermodynamic restrictions relating to the formation of the hydroxide phase than to kinetic parameters and thus it is difficult to determine quantities such as the activation energy for the carbonate formation reaction. However in the present work other kinetic parameters are examined and discussed in terms of the proposed model of the reaction.

Experimental

Changes in sample weight during absorption were recorded continuously using a Sartorius microbalance and an absorption plot was obtained on a Servoscribe recorder. The microbalance was connected to a completely greaseless vacuum system where water vapour was introduced from a thermostatically regulated distilled water reservoir and CO\(_2\) could be added from storage bulbs. All zinc oxide samples were prepared together by decomposition of basic zinc carbonate in air at 250 °C and each sample was subjected to a three hour outgassing period at 150 °C at 10\(^{-3}\) torr in the microbalance before the start of the absorption experiment. Surface area determination according to the BET method showed the zinc oxide to have a surface area of 150 sq.m./g. In all experiments the zinc oxide was first of all allowed to come to equilibrium with water vapour before carbon dioxide was introduced into the system. A convention is adopted where \(a\) is the fraction of oxide converted to hydroxycarbonate at a reaction time \(t\) and is equal to zero at the point when the CO\(_2\) is admitted to the ZnO–H\(_2\)O system.

Requests for reprints should be sent to Dr. M. F. O’Connor, Institut für Anorganische Chemie der Universität, D-8000 München 2, Meiserstraße 1.
Results and Discussion

The reaction conditions which resulted in the fastest reaction rate vary slightly from those found using a flow system. Although as before a reaction temperature of 25 °C and water vapour pressure of 21 torr were found to be optimal, a CO₂ pressure of 70 torr gave rise to the fastest reaction rate. It was attempted to fit several absorption models to the reaction and although no model could be found to fit over the whole course of the reaction, a contracting sphere model fitted very well for values of \( a \) between 0.15 and 0.5 for optimum reaction conditions. This means that in this phase of the reaction the radii of the hydroxycarbonate nuclei are expanding linearly with time and the experimentally determined \((1-a)^{1/3}\) against \( t \) plots show a straight line dependence. The initial reaction region, \( a < 0.15 \), can be considered as a combination of the equilibration of the ZnO-H₂O-CO₂ surface system and the solid state carbonate nucleation reaction. For \( a > 0.5 \), where the hydroxycarbonate phase is more than half complete, it is possible that diffusion effects, most probably concerning the transport of CO₂ to the reaction interface, begin to play a dominant role.

In order to determine the order of reaction with respect to CO₂ pressure, a series of experiments were conducted where the water vapour pressure and sample temperature were held constant and the carbon dioxide pressure was altered. The results are presented in graphical form in Fig. 1. Here \( m \) is the gradient of the straight line portion of the \((1-a)^{1/3}\) against \( t \) plots obtained for the different CO₂ pressures (\( P_{CO_2} \)). The reaction was found to obey first order kinetics with respect to CO₂ over the CO₂ pressure range 25 to 70 torr. For CO₂ pressures between 70 and 140 torr (log \( P_{CO_2} \) is between 1.85 and 2.15), the reproducibility of the reaction curve is considerably reduced and for CO₂ pressures above 140 torr, the reaction enters a third phase. On looking at the \((1-a)^{1/3}\) against time plots themselves (see Fig. 2), it can be seen that they also fall into three different types according to the three

![Fig. 1. Plot of log \( m P_{CO_2} \) against log \( P_{CO_2} \) for the zinc hydroxycarbonate formation reaction. \( P_{CO_2} \) is the pressure of carbon dioxide over the sample and \( m \) is the gradient of the reaction \((1-a)^{1/3}\) against \( t \) plot.](image1)

![Fig. 2. The three different types of \((1-a)^{1/3}\) against \( t \) plots obtained for the zinc hydroxycarbonate formation reaction depending on CO₂ pressure.](image2)

- a: CO₂ pressure > 140 torr,
- b: CO₂ pressure between 70 and 140 torr,
- c: CO₂ pressure < 70 torr.
different regions of CO₂ pressure described above. For CO₂ pressures up to 70 torr, the reaction rate is proportional to the CO₂ pressure in the gas phase and hence to the amount of CO₂ available at the reaction interface assuming that CO₂ transport to that interface presents no problem. The absorption curve can be seen to have well-defined nucleation, growth and decay periods for this CO₂ pressure region, typical for a reaction where the reaction rate is dependent upon the progression of the reaction interface to the centre of the particle. For carbon dioxide pressures above 140 torr, the \((1-a)^{1/3}\) vs time plots take a rather different form which can be understood in terms of a diffusion-controlled reaction. The rather irreproducible portion of the graph in Fig. 2 could then be explained in terms of the competition between factors dominant in the low and high CO₂ pressure regions.

The dependence of the reaction rate on water vapour pressure was investigated for temperatures between 20 °C and 40 °C and in all cases it was found that pressures close to saturated water vapour pressure were necessary before a measurable reaction rate resulted. The reaction rate decreased dramatically when the relative water vapour pressure fell below 0.8 (see Table I). It would thus seem that a nearliquid surface film of water is a necessary precondition to the reaction, its presence promoting the formation of the surface hydroxide phase previously suggested.

Table I. Dependence of the rate of the zinc hydroxy-carbonate formation reaction on the relative water vapour pressure.

<table>
<thead>
<tr>
<th>Relative water vapour pressure</th>
<th>Reaction rate ([\text{sec}^{-1}] \times 10^{4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.93</td>
<td>3.65</td>
</tr>
<tr>
<td>0.88</td>
<td>2.80</td>
</tr>
<tr>
<td>0.80</td>
<td>2.13</td>
</tr>
<tr>
<td>0.76</td>
<td>0.70</td>
</tr>
<tr>
<td>0.73</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Reaction temperature = 26.7 °C; CO₂ pressure = 60 torr.

It is clear that in such water-rich conditions it is difficult to determine whether we are dealing with a solid-gas or solid-liquid reaction. As the carbon dioxide is admitted to the ZnO–H₂O system it cannot directly adsorb onto the zinc oxide surface but must first of all dissolve in the water layer giving rise to loosely-hydrated CO₂ molecules and establishing the equilibria

\[
\begin{align*}
    \text{H}_2\text{CO}_3 &= \text{HCO}_3^- + \text{H}^+ \\
    \text{HCO}_3^- &= \text{CO}_3^{2-} + \text{H}^+
\end{align*}
\]

Due to the basic nature of the surface water film, the concentration of HCO₃⁻ ions will be greater than that of CO₃²⁻ and the CO₃²⁻ ions present will be constantly converted to barely soluble carbonate. It is therefore probable that it will mainly be the HCO₃⁻ ion which diffuses to the reaction interface and reacts with the preformed zinc hydroxide layers to form the final hydroxycarbonate.

A series of experiments were conducted where ammonia gas was introduced into the system after the surface water reaction had come to equilibrium but before the carbon dioxide had been introduced. Fig. 3 shows how the rate of the hydroxycarbonate formation reaction was influenced by the presence of ammonia gas.

![Graph showing the dependence of the rate of the hydroxycarbonate formation reaction on the pressure of ammonia gas in the reaction system.](image)
of ammonia gas. The increase in the reaction rate as
the pressure of ammonia gas in the system is
increased can be understood in terms of the effects
of the presence of ammonia on the CO$_2$/H$_2$O
equilibrium. The ammonia reacts with the H$^+$ ions
in the surface water film enabling the concentration
of HCO$_3^-$ ions to remain large. The alkaline pH of
the solution allows more CO$_2$ to be dissolved and as
a result more to be transported to the reaction
interface, leading to a faster reaction rate.

The author is indebted to Professor Dr. H. P.
Boehm for the provision of research facilities and
for his helpful advice. The Royal Society is grate­
fully acknowledged for the award of a European
Research Fellowship and Mr. P. Sharples is
thanked for his assistance with the experimental
work.

1 J. Zawadski, Festkr. J. Arvid Hedvall 54, 611 [1948].
2 W. D. Spencer and B. Topley, Trans. Faraday
Soc. 27, 94 [1931].
3 J. H. Taylor and A. Amberg, Canad. J. Chem. 39,
535 [1961].
4 N. Matsushita and D. Nakata, J. Chem. Phys. 32,
982 [1960].
5 R. J. Kokes and R. Glemza, J. Phys. Chem. 69 (1),
17 [1965].
6 P. A. Barnes, F. S. Stone, and M. F. O'Connor, J.
7 K. Atherton, G. Newbold and J. A. Hockey,
Disc. Faraday Soc. 52, 33 [1971].
Japan, 47 (1), 92 [1974].