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Note

Thermal studies on lead(II) salts

Part 4. The thermal decomposition of phosgenite, lead chloride carbonate $Pb_2Cl_2CO_3$

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Lead(II) chloride carbonate and its naturally occurring analogue phosgenite have received little attention apart from some mineralogical description. De Schulten[1] studied its thermal decomposition as did Beck[2], as part of an extensive study of carbonate minerals. They agreed on the general decomposition into an oxide chloride and carbon dioxide. Näsänen[3], in the most recent work, suggested a decomposition temperature of about 535 K and melting of the residue at about 690 K.

EXPERIMENTAL

Sample preparation

Powdered lead(II) chloride (55.6 g) was added to sodium hydroxide solution (8 g in 0.5 l) with stirring .Carbon dioxide was passed through this mixture for several days until the pH fell to 3.5. The white solid was filtered, washed and dried under vacuum, and identified by chemical analysis (Pb: found = 8.2%, calculated = 8.05%; chloride: found = 12.9%, calculated = 13.0%). The X-ray diffraction pattern was in excellent agreement with those published by Kingsbury[4] and Midgley[5].

Thermal decomposition

50 mg samples were heated in an all glass apparatus which was designed so that pre-heated purge gas could pass over the sample. The temperature was maintained by an electric furnace and controller which was operated isothermally. The temperature range studied 565 to 615 K. All samples had a particle size $<250\ \mu m$, obtained by sieving. Furnace atmospheres were varied between pure carbon dioxide and pure nitrogen by mixing metered flows of each gas at a total flow-rate of $0.2\ l\ min^{-1}$. A few runs were tried with other sample weights with no noticeable differences.

Enthalpy measurements

A DuPont 950 thermal analyser with a calorimeter module was used to determine the enthalpy of decomposition. Sapphire was used as the calibration standard[6] and the values quoted are the average of three runs.

RESULTS AND DISCUSSION

Products

Experimental weight changes (4.25%) indicated the expected loss of carbon dioxide, suggesting the overall decomposition as follows:

$$Pb_2Cl_2CO_3 = PbCl_2 \cdot PbO + CO_2 \qquad (1)$$

However, the X-ray diffraction pattern could be interpreted as a combination of the patterns from two other known oxide chlorides[7], $3PbCl_2 \cdot 2PbO$ and $PbCl_2 \cdot 2PbO$, rather than that given in eqn (1). The problems associated with the characterisation of the reaction product have been discussed elsewhere[8] and the most likely interpretation is in terms of a mixed reaction product:

$$4Pb_2Cl_2CO_3 = 3PbCl_2 \cdot 2PbO + PbCl_2 \cdot 2PbO + 4CO_2$$

KINETICS

Treatment of results

Isothermal weight-loss vs. time curves were interpreted by the method of reduced time plots, based on the time for 50% reaction[9]. The experimental reduced time plots were compared with models based on nucleation and growth-, phase

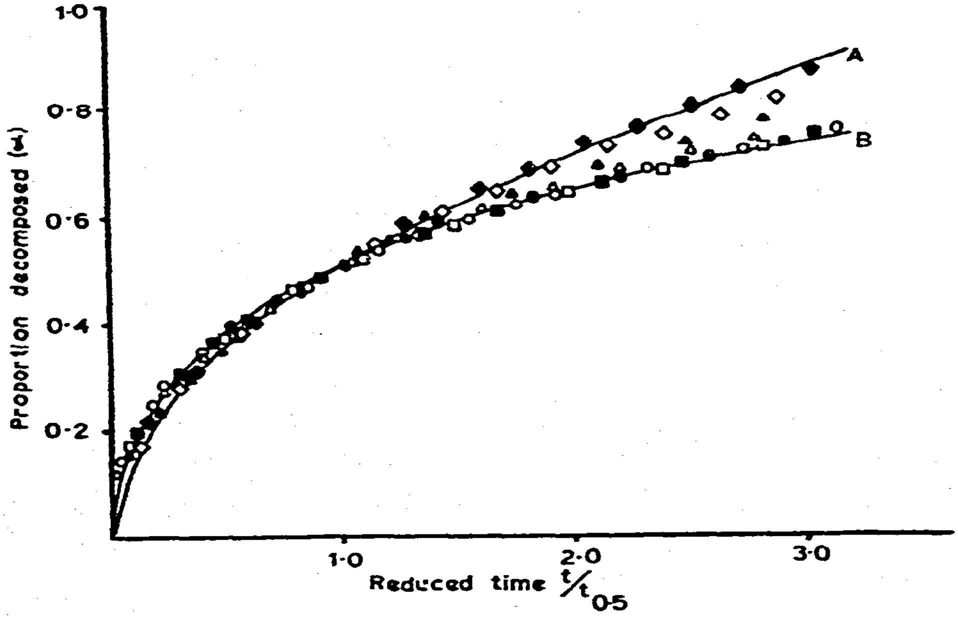

Fig. 1. Reduced time plots for thermal decomposition of lead(II) chloride carbonate. △ P_{CO_2} = 0.0 kNm^{-2}, T = 565 K; ▲ P_{CO_2} = 20.3 kNm^{-2}, T = 565 K; ◇ P_{CO_2} = 40.5 kNm^{-2}, T = 565 K; ◆ P_{CO_2} = 101.3 kNm^{-2}, T = 565 K; ○ P_{CO_2} = 0.0 kNm^{-2}, T = 580 K; ● P_{CO_2} = 81.1 kNm^{-2}, T = 580 K; □ P_{CO_2} = 40.5 kNm^{-2}, T = 592 K; ■ P_{CO_2} = 60.8 kNm^{-2}, T = 631 K. Curve A: Parabolic law, $\alpha^2 = kt$; curve B: Jander's equation, $(1-(1-\alpha)^{1/3})^2 = kt$.

boundary- or diffusion-control of the rate-controlling step. This comparison allowed the most likely mechanism of the reaction to be decided so that rate constants could be calculated.

Mechanisms

At temperatures between 613 and 580 K the best fit between experimental and calculated reduced time plots was in terms of Jander's equation[10], $(1-(1-\alpha)^{\frac{1}{3}})^2 = kt$, and a comparison is shown in Fig. 1.

In nitrogen, at the lowest temperature studied (565 K), the best fit was in terms of the parabolic law, $\alpha^2 = kt$, and at this temperature the mechanism varied considerably with the partial pressure of carbon dioxide, tending towards the higher temperature behaviour with increasing partial pressure. These effects are also shown in Fig. 1.

At the higher temperatures sintering of the product was observed, and this became more pronounced with increase in temperature till the sample could be removed as a pellet.

Rate constants which decreased with increasing carbon dioxide pressure, were calculated from the 'best-fit' mechanisms and these were used to calculate Arrhenius parameters which are given in Table 1.

TABLE 1

ARRHENIUS PARAMETERS

Partial pressure of carbon dioxide ($kN\ m^{-2}$)	*Activation energy* ($kJ\ mol^{-1}$)	*Frequency factor A* (sec^{-1})
101	215	7×10^{16}
81	200	4×10^{15}
61	182	1.5×10^{14}
41	166	7×10^{12}
20	156	1×10^{12}
0	130	8×10^{9}

Enthalpy of decomposition

The reaction enthalpy in nitrogen was calculated as 69 kJ mol^{-1} averaged over three runs. The enthalpies of formation of the two oxide chlorides assumed to be formed have been calculated[13]. Using these values and the measured enthalpy of decomposition, a value for the enthalpy of formation of phosgenite can be calculated. This value is -62.4 kJ mol^{-1} at 600 K.

Effects of temperature and carbon dioxide pressure on reaction mechanism

It is obvious from the results given that within the temperature range studied the rate of decomposition is controlled by diffusion of carbon dioxide. Figure 1 shows that variation in external pressure, at least at the lowest temperature, has an effect on the formal geometry of the process, and increase in temperature causes the same change in geometry. Jander's equation, which gives the best fit with the experimental data at higher temperatures, has several short-comings in describing solid state reactions, in that it assumes an equality in specific volumes of reactant and product and spherical particles of uniform size. It is these generally unrealistic assumptions which make the equation suspect, but in this case the fit between experiment and model is so good that it must reflect some changes in the solid which is decomposing. It is considered that the sintering noticed at higher temperatures has some bearing on the change in mechanism, in that the reaction product which forms a uniform layer round the teactant may partially melt or at least sinter to produce the very uniform diffusion implied by the Jander equation. The lowest temperature studied (565 K) is well above 0.5 T_m, at which temperature bulk diffusion is assumed to become important. A similar effect has been noted[11] when CaO reacts with CO_2.

Effect of temperature on reaction rate

The Arrhenius parameters given in Table 1 both show an increase with increase in carbon dioxide pressure. The range of activation energies is well within the range of published values for such processes. The frequency factors lie across the value normally associated with a free gaseous molecule ($\sim 10^{13}$) and the changes indicate a gradual increase in the number of degrees of freedom for the transition state[12]

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