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THERMAL STUDIES OF LEAD(II) SALTS, VI.
Kinetics of decomposition of lead(II) carbonate and lead(II) hydroxide carbonate (white lead)

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The kinetics and mechanisms of the thermal decomposition of lead(II) carbonate and lead(II) hydroxide carbonate have been studied over a range of temperatures and partial pressures of carbon dioxide using both isothermal and programmed heating. All stages in each decomposition are diffusion controlled and Arrhenius parameters have been determined. These values for loss of carbon dioxide are all extremely high for a diffusion process, but show a compensation effect, following the equation:

$$\log A = -5.02 + 0.067\,E$$

The compensation effect is discussed and comparisons with other systems showing such effects are made.

The thermal decomposition of lead(II) carbonate has been studied extensively and a large number of oxycarbonate intermediates has been postulated. The likely decomposition sequence is as follows [1]:

$$6\,PbCO_3 = 3\,(PbCO_3 \cdot PbO) + 3\,CO_2 \quad (1)$$

$$3\,(PbCO_3 \cdot PbO) = 2\,(PbCO_3 \cdot 2\,PbO) + CO_2 \quad (2)$$

$$2\,(PbCO_3 \cdot 2\,PbO) = 6\,PbO + 2\,CO_2 \quad (3)$$

A recent study [1] of the decomposition suggested that the rate of decomposition of the first intermediate, $PbCO_3 \cdot PbO$ (i.e. reaction (2)) is very dependent on the partial pressure of carbon dioxide round the sample and variation in this pressure could give rise to spurious weight losses.

The decomposition of lead(II) hydroxide carbonate (white lead) has been less studied than that of the simple carbonate. The most likely decomposition scheme [2] is as follows:

$$2\,(2\,PbCO_3 \cdot Pb(OH)_2) = 2\,(2\,PbCO_3 \cdot PbO) + 2\,H_2O \quad (4)$$

$$2\,(2\,PbCO_3 \cdot PbO) = 3\,(PbCO_3 \cdot PbO) + CO_2 \quad (5)$$

$$3\,(PbCO_3 \cdot PbO) = 2\,(PbCO_3 \cdot 2\,PbO) + CO_2 \qquad (6)$$

$$2\,(PbCO_3 \cdot 2\,PbO) = 6\,PbO + 2\,CO_2 \qquad (7)$$

The present work involves the determination of reaction mechanisms and Arrhenius parameters for the reactions given above, over a range of temperatures and partial pressures of carbon dioxide.

Experimental

Starting materials

These were prepared and characterised as previously described [1, 2].

Thermal decomposition

An electrobalance (CI Microforce, Mark 2C), sensitivity 10 mg fsd, attached to a potentiometric recorder was used throughout the work. An electric furnace was controlled by a Stanton Redcroft Eurotherm controller. The temperature was monitored by a thermocouple located ~ 1 mm below the sample container. The controller was used to give linear programmed heating with rates from 0.5–5.0 degree min^{-1} or to give isothermal control to a probable accuracy of ±1 degree.

The temperature-programmed mode was used to prepare the various intermediates by heating samples at 5 degree min^{-1} until the correct weight loss had been obtained. The intermediates were then heated isothermally to determine reaction mechanisms and Arrhenius parameters. Kinetic data were also obtained from programmed heating runs using a heating rate of 2 degree min^{-1}.

Atmosphere control

Furnace atmospheres were varied between nitrogen (99.9%) and carbon dioxide (99.9%), both of which were dried over silica gel and magnesium perchlorate before passing over the sample. Each gas stream was metered separately and the total flow was 0.2 $dm^3\ min^{-1}$. The total pressure was always one atmosphere.

Results

Isothermal heating

The results for all runs were tested by comparison of the experimental reduced-time plots, based on the time for 50% reaction (α *vs.* $t/t_{0.5}$, where α = proportion reacted), with those for various models based on nucleation and growth control, phase boundary control and diffusion control of the decomposition [3]. All of the weight-loss curves were deceleratory and with a single exception the best fit between experiment and model data was in terms of the parabolic law, $\alpha^2 = kt$. This suggests a diffusion process as the rate controlling step. Typical results showing the agreement are shown in Figs 1 and 2.

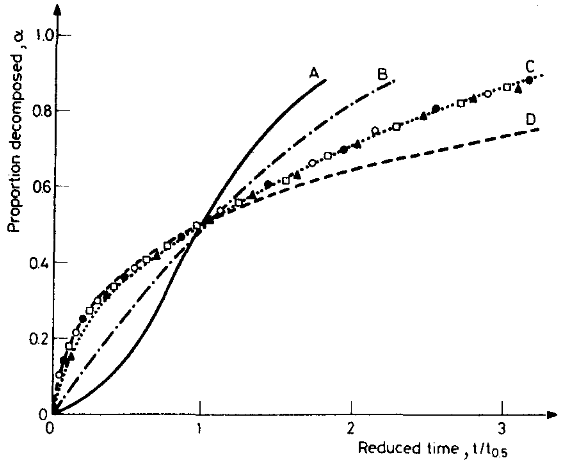

Fig. 1 Reduced-time plots for the isothermal decomposition of lead(II) carbonate. ○ reaction 2: 610 K, P = 0.80 atm., ● reaction 2: 620 K, P = 0.2 atm., ▲ reaction 3: 610 K, P = 0.025 atm., □ reaction 3: 700 K, P = 1.0 atm. Curve A: $-\ln(1-\alpha)^{1/2} = kt$, B: $1-(1-\alpha)^{1/2} = kt$, C: $\alpha^2 = kt$, D: $(1-(1-\alpha)^{1/3})^2 = kt$

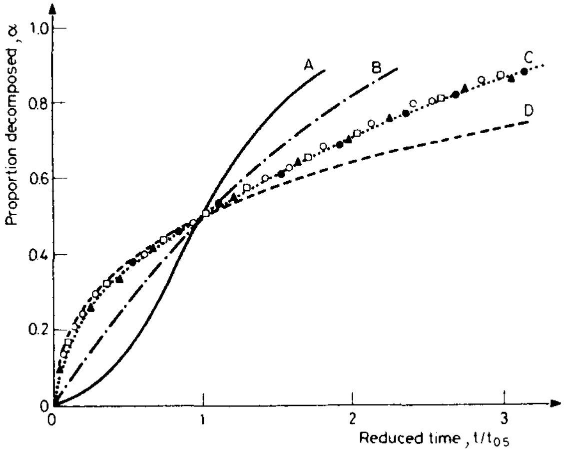

Fig. 2 Reduced-time plots for the isothermal decomposition of lead(II) hydroxide carbonate. ○ reaction 4: 400 K, P = 0.6 atm., ● reaction 5: 500 K, P = 0.1 atm., ▲ reaction 6: 670 K, P = 1 atm., □ reaction 7: 720 K, P = 1 atm. Curve A: $-\ln(1-\alpha)^{1/2} = kt$, B: $1-(1-\alpha)^{1/2} = kt$, C: $\alpha^2 = kt$, D: $(1-(1-\alpha)^{1/3})^2 = kt$

The first stage of the decomposition of lead carbonate (reaction (1)) gave reduced time plots which did not fit any of the models used. The experimental plots indicate a much faster early decomposition than predicted and is typical of decomposing solids in which there is a wide range of particle size [4]. The effect was eliminated by sieving out the larger crystals. Changes in shape of the reduced-time plots for various particle sizes are shown in Fig. 3. As a consequence of this, sieved material was used throughout.

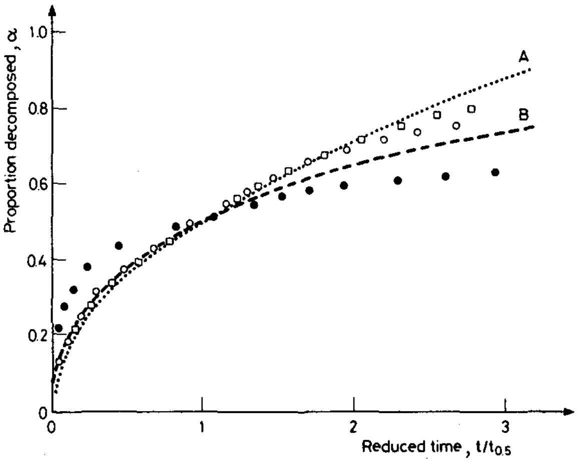

Fig. 3 Variation of reduced-time plot with particle-size distribution for stage 1 in lead carbonate decomposition. ● ≤ 250 μm, ○ ≤ 150 μm, □ ≤ 100 μm. Curve A: $\alpha^2 = kt$, B: $(1 - (1 - \alpha)^{1/3})^2 = kt$

Isothermal data were collected for every stage in each decomposition, over a wide range of carbon dioxide partial pressure, where this was possible so that each reaction mechanism could be decided on. In addition, a range of temperatures was studied to determine Arrhenius parameters. These are given in Tables 1 and 2, and are considered to be accurate to ±7%.

Temperature programmed heating

The programmed runs were analyzed by means of the extended Coats and Redfern method [5]. The same mathematical models were used as for the isothermal data and the model which gave the best straight line fit to the experimental data was considered to be correct. The naive use of least squares routines to decide on the best straight line caused some problems which were over-come by knowledge of the rate-controlling step from the isothermal work [6]. Values of α between 0.1 and 0.9 were used throughout the calculations. Arrhenius parameters calculated in this way are given in Tables 3 and 4, and are accurate to ±10%.

Table 1 Arrhenius parameters as a function of partial pressure of carbon dioxide – lead(II) carbonate decomposition. Isothermal heating

p_{CO_2}, kNm^{-2}	Reaction 1		Reaction 2		Reaction 3	
	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}
101.3	444	35.21	699	51.42	980	64.92
81.1	429	34.44	637	50.73	927	64.71
20.3	372	31.93	367	29.81	874	59.82
2.5	355	29.76			664	55.82
0.0					428	44.71

Table 2 Arrhenius parameters as a function of partial pressure of carbon dioxide – lead(II) hydroxide carbonate. Isothermal heating

p_{CO_2}, kNm^{-2}	Reaction 4		Reaction 5		Reaction 6		Reaction 7	
	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}
101.3	40	4.83	487	46.01	1100	91.01	1327	95.11
60.8	36	4.79	490	45.13	1197	90.02	1342	95.72
20.3	39	4.29	470	46.83	1082	81.76	1257	86.01
10.1	35	4.54	466	44.53	972	80.61		
5.1					972	79.02	762	55.82
2.5	44	4.11	452	42.69				
0.0	46	3.07	329	31.75				

Table 3 Arrhenius parameters as a function of partial pressure of carbon dioxide—lead carbonate. Programmed heating

p_{CO_2},	Reaction 1		Reaction 2		Reaction 3	
kNm^{-2}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}
101.3	473	38.36	663	50.65	930	67.36
81.1	456	36.90	655	50.11	950	66.52
60.8	435	35.54	597	48.89	920	65.79
50.7	441	36.26	557	42.58	894	63.43
40.5	408	32.36	458	34.04		
20.3	398	33.26	380	30.18	850	60.67
10.1	400	30.99	339	27.26	803	57.88
2.5	360	32.48			701	56.00
0.0					406	45.43

Table 4 Arrhenius parameters as a function of partial pressure of carbon dioxide—lead hydroxide carbonate. Programmed heating

p_{CO_2},	Reaction 4		Reaction 5		Reaction 6		Reaction 7	
kNm^{-2}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}	E, kJ mol^{-1}	log A, sec^{-1}
101.3	38	4.62	502	45.43	1247	91.18	1402	96.23
81.1	42	4.34	527	48.94	1230	90.70	1439	97.15
60.8	38	4.62	510	46.54	1239	91.60	1430	98.49
40.5	38	4.18	502	46.43	1188	87.86	1305	90.08
20.3	42	4.23	510	47.18	1113	82.95	1222	85.60
10.1	33	4.65	485	45.15	1080	81.70	1054	74.85
5.1	42	3.81	477	44.54	1063	81.89	795	56.30
2.5	42	4.08	469	43.91	1004	77.48	619	44.81
0.0	50	2.80	352	32.04				

Discussion

Isothermal reaction mechanisms

The evidence presented indicates that a diffusion process is the rate controlling step in all of the stages of decomposition. The obedience of the experimental data to the parabolic law suggests that the diffusion is one-dimensional and since both starting materials have a plate-like habit, it is likely that diffusion will be occurring along the shortest dimension. The apparent change in mechanism for unsieved lead carbonate is almost certainly caused by aggregation of particles, as is shown by SEM. These aggregates are preferentially removed or broken down by sieving.

Arrhenius parameters

Examination of the tables shows that, for most of the reactions studied, the activation energies and frequency factors are very high indeed for a diffusion process. The only reaction to which this does not apply is the dehydroxylation of the hydroxide carbonate (reaction (4)). For this reaction the activation energy is around 40 kJ mol^{-1} and is largely independent of the external pressure of carbon dioxide. This value is within the range expected for diffusion of water [7]. The frequency factor is low and indicates the loss of degrees of freedom in the transition state, relative to an isolated gaseous molecule, which may be caused by the involvement of a surface.

The Arrhenius parameters for all the reactions involving loss of carbon dioxide are much higher than those for loss of water. Most of these values are high for any possible kinetic process; commonly used models [8] do not derive frequency factors higher than about 10^{18}. The high Arrhenius parameters are not a function of the experimental method used to generate the data, since both isothermal and TG results agree where the comparison can be made. Such agreement suggests that the high values have a chemical basis, rather than an experimental one.

It is apparent also from Tables 3 and 4 that the Arrhenius parameters for identical reactions (2 and 6; 3 and 7) differ widely, with the lead carbonate series belong lower than those for white lead. Such kinetic differences between different preparations of similar solids are common and difficult to account for except in general terms. Differences in crystal structure and morphology in the starting compounds will affect the physical properties of the decomposition products. Such differences could be particularly important for a diffusion controlled process.

Given that the reactions under discussion are similar in terms of chemistry and kinetics, it is difficult to assign the experimental Arrhenius parameters to a simple diffusional loss of carbon dioxide. However there is a sympathetic variation between E and A, which has been called the compensation effect [9], and Fig. 4 which illustrates the effect further, has been called a compensation plot.

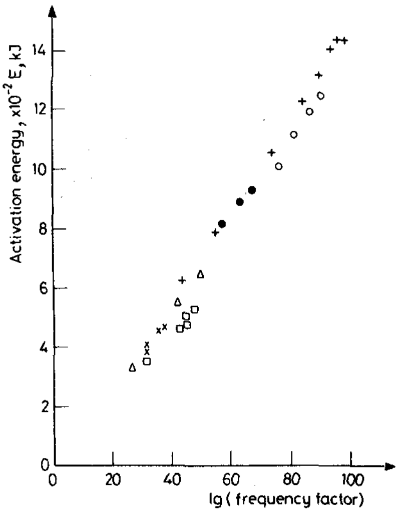

Fig. 4 Compensation plot showing log *A* *vs.* *E* for decompositions (TG results). x reaction 1, △ reaction 2, ● reaction 3, ○ reaction 5, □ reaction 6, + reaction 7

The compensation effect

Compensation effects are well known in both homogeneous and heterogeneous kinetics; catalyst kinetics have been recently discussed by Galwey [9]. The effect is commonly discussed in terms of bond rearrangement but can also occur in diffusion controlled reactions [10].

The usual mathematical description of the effect is to state that a series of Arrhenius parameters obey the equation

$$\log A = B + eE$$

where A and E are the frequency factor and activation energy and B and e are constants, the 'compensation parameters'. For some homogeneous systems e seems to approach unity, but there is greater variation in heterogeneous systems. A recent statistical survey [11] of mean compensation parameters for heterogeneous catalyst reactions has shown that for such systems the parameters lie within rather narrow limits:

$$16.6 < B < 19.0, \quad 0.099 < e < 0.118$$

The values of B and e calculated from Fig. 4, assuming that all values lie about a single line are $B = -5.02$, $e = 0.067$ and are therefore very different from those for typical catalyst reactions studied by Galwey and Brown [11]. These obviously reflect differences in the fundamental chemical processes occurring. Compensation parameters for the decomposition of calcium carbonate have also been obtained [12]. Greater understanding of the compensation effect can be gained by consideration of the differences between homogeneous and heterogeneous reactions. In a homogeneous series of consecutive reactions, involving reactants (R), products (P), and intermediates (I):

$$R \rightarrow I(1) \rightarrow I(2) \rightarrow I(x) \rightarrow I(y) \rightarrow P$$

the rate at each stage is governed by the number of activated complex molecules passing over an energy barrier, with the slowest step (say $I(x) \rightarrow I(y)$) governing the overall rate. The total number of activated complex molecules, and therefore $\{I(x)\}$ is limited only by the reaction temperature and the various energy terms, since each step is governed by an Arrhenius equation, Rate $= A \exp(-E/RT)$.

If the reaction involves a reaction interface, however, and the intermediate stages all involve active surface sites then an additional constraint may enter the overall kinetics. If the total number of active sites is limited, then this number may become a bottle-neck to reaction and the concentration of any intermediates is not solely dependent on the reaction temperature and Arrhenius parameters.

For the heterogeneous rate-controlling step, $I(x) \rightarrow I(y)$, the rate is not only dependent on the Arrhenius parameters but also on the proportion of the active sites occupied by $I(x)$, i.e. $[I(x)]/N_{TOT}$, where N_{TOT} = number of active sites. The equilibria involving $I(x)$ and all other intermediates with the limited number of active sites will introduce a temperature dependence for the reaction which will differ from that shown by a homogeneous reaction, or that shown by a heterogeneous reaction in which the number of active sites is not limited. The most important effect of the limit on active sites is to reduce the rate of the slowest step by reducing $[I(x)]$. Galwey has shown numerically [13] that for a reaction with $A = 3.2 \times 10^{30}$ molecules sec^{-1} and $E = 100$ kJ mol^{-1}, variation in $[I(x)]$ by a factor of $10^{\pm 3}$ causes variation in $\log A$ between 10^{20} and 10^{45} and in E between 0 and 250 kJ mol^{-1}. Low concentrations of $I(x)$ produce high values of A and E.

Such equilibria involving active sites are commonly controlled by bond-making or bond-breaking processes, e.g. catalytic processes in which sorption energies contribute to the overall energy balance. It is also possible however, that such active sites and sorption energies are involved in diffusion-controlled reactions, by limiting the mobility of the diffusing species. Such limited mobility is, of course, dependent on specific interactions between diffusing species and substrate.

Pressure dependence of Arrhenius parameters

Examination of the results given in the tables indicates an increase in A and E with increasing partial pressure of carbon dioxide; the effect is logarithmic rather than linear. Such increases in A and E suggest, from Galwey's analysis [13], that the concentration of rate controlling intermediates is being reduced. This would happen if normal dynamic equilibrium existed between atmospheric carbon dioxide and the postulated active sites on the various oxycarbonate intermediates.

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We wish to record our thanks to Dr. A. K. Galwey for his interest and the considerable time he has spent discussing the general and particular problems of the compensation effect.

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Zusammenfassung — Kinetik und Mechanismus der thermischen Zersetzung von Blei(II)carbonat und Blei(II)hydroxycarbonat wurden bei verschiedenen Temperaturen und CO_2-Partialdrücken sowohl isotherm als auch unter den Bedingungen der programmierten Aufheizung untersucht. Bei allen Zersetzungsschritten ist die Diffusion der geschwindingkeitsbestimmende Schritt; die Arrhenius-Parameter wurden bestimmt. Für einen Diffusionsprozess sind diese Werte extrem hoch, sie zeigen aber einen durch die Gleichung

$$\log A = -5.02 + 0.067\,E$$

zu beschreibenden Kompensationseffekt, der diskutiert wird. Durch Vergleich mit anderen Systemen wird gezeigt, wie solche Effekte zustande kommen.

Резюме — Изучена кинетика и механизм термического разложения карбоната- и гидроксикарбоната свинца в широкой области температур и парциальных даблений двуокиси углерода, используя изотермический и программированный нагрев. Все стадии каждого разложения являются диффузионно-контролируемыми и для которых определены параметры Аррениуса. Полученные значения потери двуокиси углерода являются экстремально высокими для диффузионного процесса, но показывают компенсационный эффект, подчиняющийся уравнению: $\log A = -5.02 + 0.067\,E$. Компенсационный эффект обсужден и сопоставлен с таковым для других систем.