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THERMAL STUDIES ON LEAD(II) SALTS

PART 3. THE DECOMPOSITION OF LAURIONITE, LEAD(II) HYDROXIDE CHLORIDE

MATTHEW C. BALL AND MICHAEL J. CASSON
Department of Chemistry, University of Technology, Loughborough, Leics., LE11 3TU (England)

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ABSTRACT

The thermal decomposition of synthetic lead(II) hydroxide chloride has been studied between 490 and 520 K over a range of partial pressures of water vapour. The reaction rate is controlled by diffusion of water vapour and Arrhenius parameters have been calculated. The activation energy varies between 92 and 145 kJ mol^{-1} and the frequency factor between 10^9 and 10^{15} sec^{-1}. Water vapour pressure has a profound effect on the reaction rate and a double minimum in the rate is observed. Enthalpimetric data are also presented for the decomposition.

INTRODUCTION

The mineral form of lead(II) hydroxide chloride, laurionite, was noted by Köchlin[1] who named it from the site. The mineral is also given the site name Matlockite. The compound has received considerable attention to determine if it is a true hydroxide salt, most recently by Yadava et al.[2], who used conductometric, potentiometric and infra-red techniques to conclude that the correct formulation was Pb(OH)Cl.

The thermal decomposition has been studied by Ramamurthy et al.[3] as part of an extensive study of metal hydroxy compounds. They derived an activation energy for the decomposition in nitrogen from isothermal studies.

The present work aims to extent Ramamurthy's work in studying the effect of varying partial pressures of water vapour.

EXPERIMENTAL

Sample preparation

A modification of the method[4] used to prepare Pb(OH)Br was used: potassium chloride solution (2.8 w/v) was slowly added to lead acetate solution (4.5 w/v) with stirring. The precipitate was filtered, washed and dried at 373 K. X-ray diffraction gave a pattern in excellent agreement with that published. Chemical analysis also gave good results: Lead found 79.67%, calculated 79.80%; chloride found 13.43%, calculated 13.65%. Infrared analysis gave results in agreement with those of Ramamurthy[3].

Thermal decomposition

100 mg samples (particle size <250 μm) were heated in an all glass apparatus which was designed so that preheated purge gas could pass over the sample. Weight losses were measured using a C.I. microforce balance and a recorder (total sensitivity 4 mg f.s.d.). Nitrogen was used as purge gas at a flow-rate of 0.2 l min^{-1} and controlled partial pressures of water vapour were obtained by passing the gas through saturated salt solutions or over drying agents. The temperature was maintained by an electric furnace and a Stanton Redcroft Linear Variable Programmer. After a few TG runs to determine the temperature range of the decomposition, the programmer was used in the isothermal mode in the range 490 to 520 K.

Other experimental techniques

Infrared spectra were measured on a Perkin-Elmer 457 using Nujol mulls and sodium chloride plates and X-ray diffraction was carried out using CuK_α radiation. Enthalpies of decomposition were measured on the calorimeter module of a DuPont 950 Thermal Analyser using sapphire as the calibration standard[5]. A sample of the basic salt was examined by electron microscopy: this showed the presence of flat plates of uniform size (~10 μm largest dimension).

RESULTS

Products

Experimental weight changes indicated the expected loss of water (3.47%) in a single step, suggesting the overall decomposition as follows:

$$2Pb(OH)Cl = PbCl_2\cdot PbO + H_2O \qquad (1)$$

However, the X-ray diffraction pattern of the product (Table 1) could be interpreted as being a combination of the patterns from two other known oxide chlorides[6,7], $3PbCl_2\cdot 2PbO$ and $PbCl_2\cdot 2PbO$. This combination would give the same overall stoichiometry as eqn (1).

These two compounds were synthesised by heating the correct molar quantities of $PbCl_2$ and PbO (at 800 K for the 3:2 compound and 1000 K for the 1:2 compound). The diffraction patterns of these preparations were in good agreement with those published (also Table 1). A 1:1 molar mixture of the 3:2 and 1:2 compounds was heated at temperatures above and below the incongruent melting point given by Renaud et al.[8] (700 and 925 K, respectively). Each mixture gave, on cooling, a diffraction pattern in good agreement with that of the decomposition product.

The infrared spectrum of the product showed only one absorption band, at 375 cm^{-1}. Lead(II) chloride showed no absorption peaks in the region scanned (250 to 4000 cm^{-1}).

The product from decompositions carried out under the lowest water vapour pressures used gave a diffraction pattern which consisted of a few broad peaks. When the product was heated in increasing partial pressures of water vapour, the peaks

TABLE I

COMPARISON OF X-RAY RESULTS

Experimental		*$3PbCl_2 \cdot 2PbO$*		*$PbCl_2 \cdot 2PbO$*	
d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0
4.33	12	4.30	40		
4.14	8			4.15	10
				4.10	10
3.92	39	3.93	60		
3.79	25			3.78	40
3.72	51	3.74	80		
3.51	31	3.58	20	3.50	60
3.43	18	3.45	20		
3.31	47	3.33	40	3.29	20
3.24	31				
3.20	12	3.21	40		
3.11	23			3.09	100
3.04	34			3.04	70
2.97	17				
2.91	54	2.91	90	2.90	40
2.80	54				
2.78	100	2.79	100	2.78	70
2.73	54	2.74	100		
2.71	23			2.71	20
2.65	39			2.64	70
				2.53	10
2.44	20	2.45	20	2.48	10
2.38	11			2.31	20
2.19	12	2.19	50		
2.17	18			2.17	40
2.14	15	2.13	50		
2.10	23			2.11	70
2.08	14	2.09	40		
2.01	23	2.01	60	2.00	10
1.961	9	1.96	40		
				1.882	50

sharpened considerably. The peaks from the 3:2 compound seemed to sharpen before those of the 1:2 compound although this was difficult to quantify.

Kinetics and mechanisms

The decomposition curves (α vs. t) were all deceleratory and were interpreted by the method of reduced time plots[9], based on the time for 50% reaction. The experimental reduced time plots were compared with model curves based on nucleation and growth control, phase boundary control or diffusion control as the rate controlling step. This comparison allowed the most likely mechanism for the reaction to be decided so that rate constants could be calculated.

Representative data over a range of water vapour pressures are illustrated in Fig. 1, together with various diffusion models for comparison. The best fit between

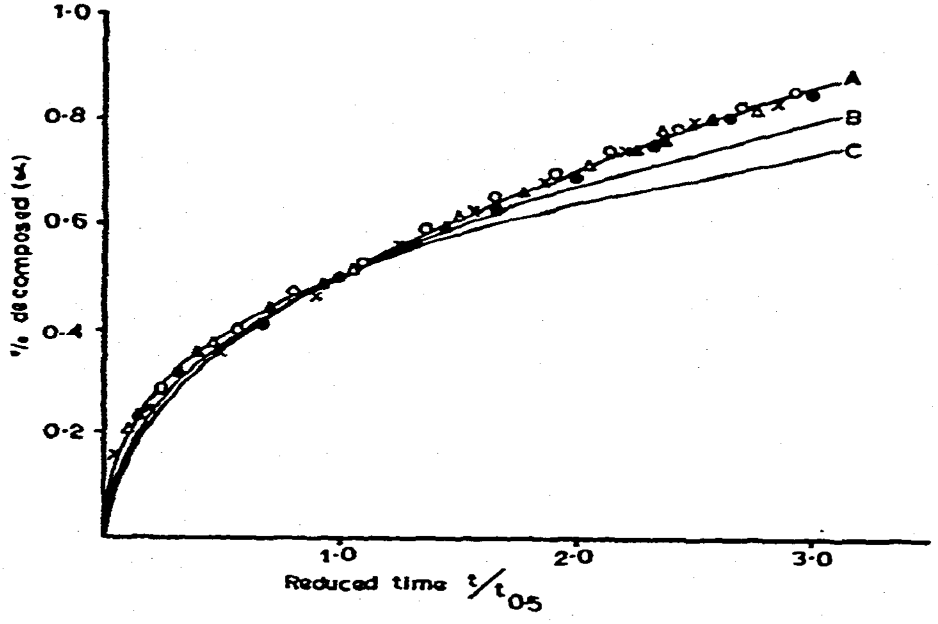

Fig. 1. Reduced-time plot for decomposition of lead(II) hydroxide chloride. ● $P_{H_2O} = 3.1$ kNm^{-2}, $T = 519$ K; ○ $P_{H_2O} = 6.7$ kNm^{-2}, $T = 519$ K; × $P_{H_2O} = 20.0$ kNm^{-2}, $T = 510$ K; △ $P_{H_2O} = 13.3$ kNm^{-2}, $T = 498$ K; ▲ $P_{H_2O} = 1.6$ kNm^{-2}, $T = 490$ K. Curve A: Parabolic law, $\alpha^2 = kt$; curve B: two-dimensional diffusion, $(1-\alpha)\ln(1-\alpha)+\alpha = kt$; curve C: Jander's equation, $(1-(1-\alpha)^{\frac{1}{3}})^2 = kt$.

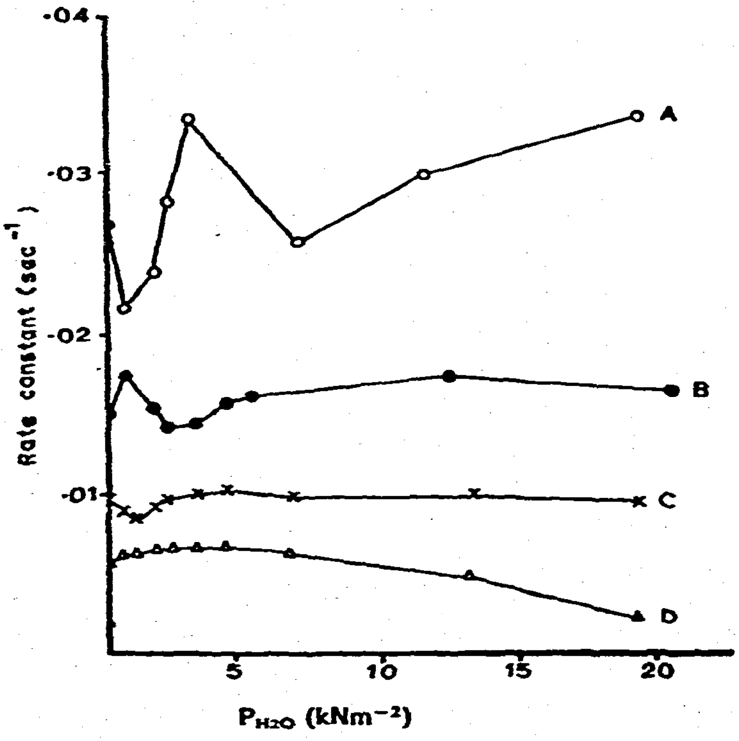

Fig. 2. Variation in rate constant with water vapour pressure. Curve A: 519 K; curve B: 510 K; curve C: 498 K; curve D: 490 K.

experimental data and model can be seen to be in terms of the parabolic law, $\alpha^2 = kt$, i.e., a one-dimensional diffusion process is probably rate controlling. Rate constants were calculated on the basis of this equation and the variation with temperature and partial pressure of water vapour is shown in Fig. 2. These rate constants were also used to calculate the Arrhenius parameters given in Table 2.

TABLE 2

ARRHENIUS PARAMETERS FOR $Pb(OH)Cl$ DECOMPOSITION

Water vapour pressure ($kN\ m^{-2}$)	*Activation energy* ($kJ\ mol^{-1}$)	*Frequency factor* (sec^{-1})
10^{-7}	145	3.0×10^{15}
0.61	92	1.2×10^{9}
1.59	99	1.5×10^{10}
2.17	108	5.7×10^{11}
3.07	121	1.5×10^{13}
4.27	96	1.1×10^{11}
6.67	100	7.8×10^{10}
13.33	115	3.7×10^{12}
20.00	128	7.5×10^{13}

Enthalpy of decomposition

A value of 25 kJ mol^{-1} was obtained for the enthalpy change. The decomposition was carried out in dry nitrogen and the result averaged over four runs.

DISCUSSION

Products

In general the simple reaction scheme has been assumed, even though Beck[10] found difficulty in characterising the product. The X-ray diffraction evidence presented here suggests that the products (at room temperature) are the two other oxide chlorides, and the decomposition should be written as follows:

$$4Pb(OH)Cl = 3PbCl_2 2PbO + PbCl_2 \cdot 2PbO + 2H_2O$$

The $PbCl_2$–PbO system has been studied by Renaud et al.[8] and their results suggest an incongruent melting point for the 1:1 compound of 751 K. Mixtures of this composition heated above and below 750 K gave the same diffraction patterns. This suggests that if the 1:1 compound exists at high temperatures, then its structure cannot be quenched under the conditions used.

Reaction mechanism

The best fit between experiment and theory in terms of the parabolic law suggests that the diffusion process is a simple one. The most likely way in which a one-dimensional process can occur in a plate is at right angles to the main crystal face.

Arrhenius parameters

The activation energies and frequency factors vary widely with water vapour pressure. The variations are, however, almost exactly parallel and will be discussed in the next section on variations in reaction rate. The numerical values of activation energy are within the range to be expected for a diffusion process. The frequency factors range from 10^9 to 10^{15}, the latter value being rather higher than that expected for a free, gaseous molecule. The low values suggest a transition state with restricted degrees of freedom such as might occur in a molecule sorbed on a surface[11].

In the only other study of the decomposition of laurionite, Ramamurthy[3] derived an activation energy of 81.6 ± 8.4 kJ mol^{-1}. This was for a decomposition in 'dry' nitrogen, without the partial pressure of water vapour being stated. It is, therefore, a little difficult to make comparisons except to note that Ramamurthy's value is lower than any obtained in the present work.

Effect of water vapour pressure on reaction rate

Figure 2 shows the wide variation in reaction rate with water vapour pressure. The commonest explanation for the occurrence of such maxima and minima is that of Topley and Smith[12], who suggested that at low pressures of water vapour an amorphous layer of product is formed which slows down the diffusion of water vapour. With increasing partial pressure of water vapour, sorption occurs which causes the amorphous product to crystallise. This better crystalline material allows diffusion to take place more easily. An extensive list of salts in which this effect has been noted is given by Quinn et al.[13]. These compounds show only a single minimum in the rate whereas the present work indicates a double minimum. This has been noted previously in the dehydration of zinc sulphate heptahydrate[14], with no explanation given. In the present case consideration was given to the possibility that the double minimum might be associated with the crystallisation, at different partial pressures of water vapour of each of the two products formed in the reaction. The X-ray study indicates the formation of an amorphous phase giving only broad diffraction peaks which sharpen on exposure to water vapour. It is likely that the 3:2 compound crystallises before the 1:2 compound.

The effect of temperature on these maxima and minima is typical, in that the variations decrease with decreasing temperature. This is the behaviour expected if sorption of water is important, since lowering of the temperature would allow more sorption which would blur the changes apparent at higher temperatures.

Enthalpy of formation of laurionite

The measured enthalpy of decomposition, when combined with the enthalpies of formation of the two oxide chlorides[9], gave an enthalpy of formation for Pb(OH)Cl of -188.2 kJ mol^{-1}.

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