KINETICS OF THE ISOTHERMAL TRANSFORMATION OF β-PbO$_2$ INTO α-PbO$_2$

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ABSTRACT

The isothermal transformation of β-PbO$_2$ into α-PbO$_2$ was studied. This process takes place at 440–450 °C and is accompanied by a decrease in the ratio Pb(IV)/(Pb(II) + Pb(IV)), although it always remains higher than 0.9. The kinetic analysis of the isothermal data shows that the activation energy of the process is ca. 150 kJ mol^{-1}. The transformation involves a two-dimensional growth of nuclei that are related to the OH content of the samples. For ground β-PbO$_2$, the higher Pb(II) and OH content causes a change in the kinetic law governing the reaction, which is described by a contracting area model.

INTRODUCTION

The polymorphism and thermal decomposition of lead dioxide have been the subject of extensive research in the past. It is well known that formation of the orthorhombic form α-PbO$_2$ by thermal treatment of the rutile form β-PbO$_2$ requires high O$_2$ pressures to avoid decomposition of the dioxide [1]. The thermal decomposition of β-PbO$_2$ at ca. 1 atm occurs in a number of steps that depend markedly on the pre-history of the sample [2] and the heating rate [3]. However, the first step is usually ascribed to the formation of α-PbO$_x$ [4].

The mechanochemical transformation of β-PbO$_2$ into α-PbO$_2$ takes place during milling at ambient pressure [5]. A recent study on the mechanochemistry of this system [6] has shown that the phase transition is accompanied by chemical changes, including an increase in Pb(II) contents and the development of OH groups. These changes limit the stability of the different intermediates in the thermal decomposition of the samples.

In this paper, the low-pressure transformation of β-PbO$_2$ containing different amounts of Pb(II) into α-PbO$_2$ under isothermal conditions is studied and the kinetic data are analyzed.

EXPERIMENTAL

A commercial high-grade β-PbO$_2$ sample (Merck) was used in the study. A fraction of this sample was mechanically activated by dry grinding in a static air atmosphere, using a planetary ball mill (Retsch). An initial sample charge of 50 g of β-PbO$_2$ and three agate balls of 10 mm in diameter were placed in a 250 ml agate jar. The sample was ground for 300 min at 70 rev min^{-1}. As the grinding time was short, no traces of α-PbO$_2$ were detected in the ground sample.

The thermal transformations of β-PbO$_2$ were studied with a Mettler TA 3000 DSC apparatus under a static air atmosphere. Sample weights of ca. 50 mg were used. Isothermal runs were carried out at different temperatures and the traces were digitalized and converted into degree of conversion by numerical integration.

The chemical compositions of the samples were determined according to the analytical procedure developed by Anderson and Sterns [7]. X-ray diffraction patterns were obtained with a Philips PW1130 diffractometer using Co $K\alpha$-radiation and an iron filter.

RESULTS AND DISCUSSION

Several isothermal runs were carried out in the DSC apparatus over a temperature interval corresponding to the first accelerating stage of the complex endothermic effect found at 400–600°C in the dynamic DSC traces of unground and ground β-PbO$_2$ samples. The isothermal traces are shown in Fig. 1. The characterization of the initial and final products of these experiments was carried out using X-ray diffraction (Fig. 2) and chemical analysis (Table 1). The diffractograms show the absence of α-PbO$_2$ in both parent samples and the complete conversion to the orthorhombic form after the isothermal run. The results in Table 1 show a slight increase in Pb(II) content with milling, proportionally smaller than that found during the mechanochemical phase transition [6]. This enhancement is related to surface activation by grinding. After the isothermal experiments, the Pb(II) contents show little change and remain, in any case, within the expected limits for both polymorphs of PbO$_2$ [8]. These results show that the thermal transformation has taken place under the experimental conditions without decomposition to α-PbO$_x$. In agreement with this observation, the shapes of the isothermal traces in Fig. 1 are consistent with a single endothermic process. This behaviour can be considered to be the limiting case of the effect of a low heating rate on the intermediate products of the thermal evolution of β-PbO$_2$ [3].

From a kinetic point of view, the shapes of the isotherms show a lack of induction period. The analysis of these data was carried out using the kinetic
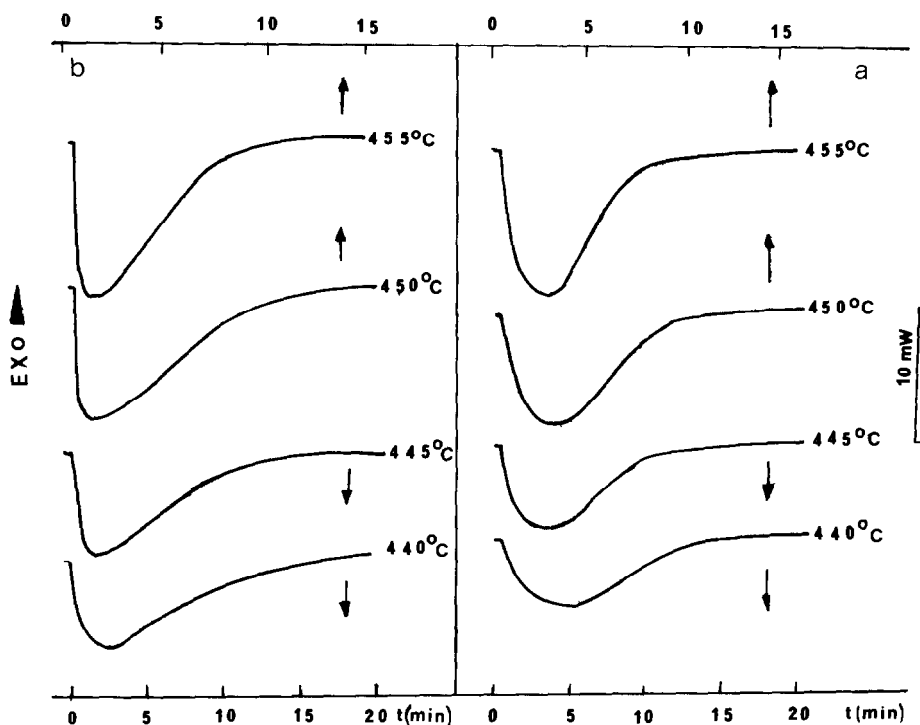
Fig. 1. Isothermal kinetic runs at various temperatures for unground and ground β-PbO$_2$.

expressions in Table 2. The experimental α values in the 0.2–0.6 range were fitted to the general equation

$$g(\alpha) = kt$$

A comparison of the linear regression coefficients obtained by least-squares fitting to the various kinetic expressions by the application of the statistical t test did not allow us to discern the operative mechanism in each case. However, Fig. 3 shows the reduced time plots for the kinetic data of

TABLE 1

Results of the chemical analyses of unground and ground β-PbO$_2$ samples and their isothermal conversion products

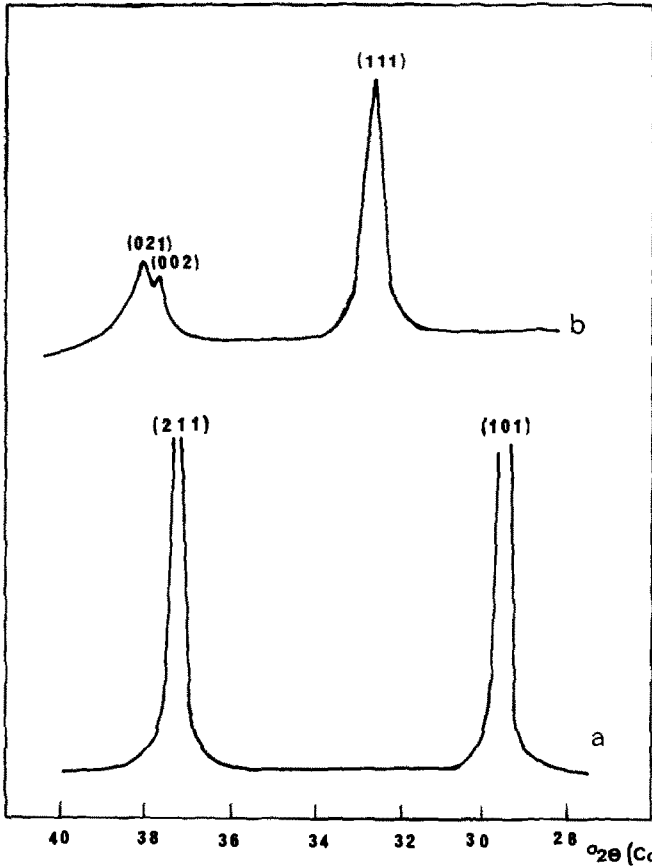| Sample grinding time (min)	Pb(IV)/(Pb(II) + Pb(IV))		
	Unheated	After isothermal run	
		445°C	450°C
0	0.978	0.952	0.954
300	0.950	0.923	0.918

Fig. 2. Selected X-ray diffraction patterns of β-PbO$_2$ and the product obtained after the isothermal runs.

unground and ground β-PbO$_2$. From these plots, it seems that neither the diffusion kinetic laws nor the first-order mechanism accurately describes the kinetic data.

TABLE 2

Algebraic functions $g(\alpha)$ used in the kinetic analysis

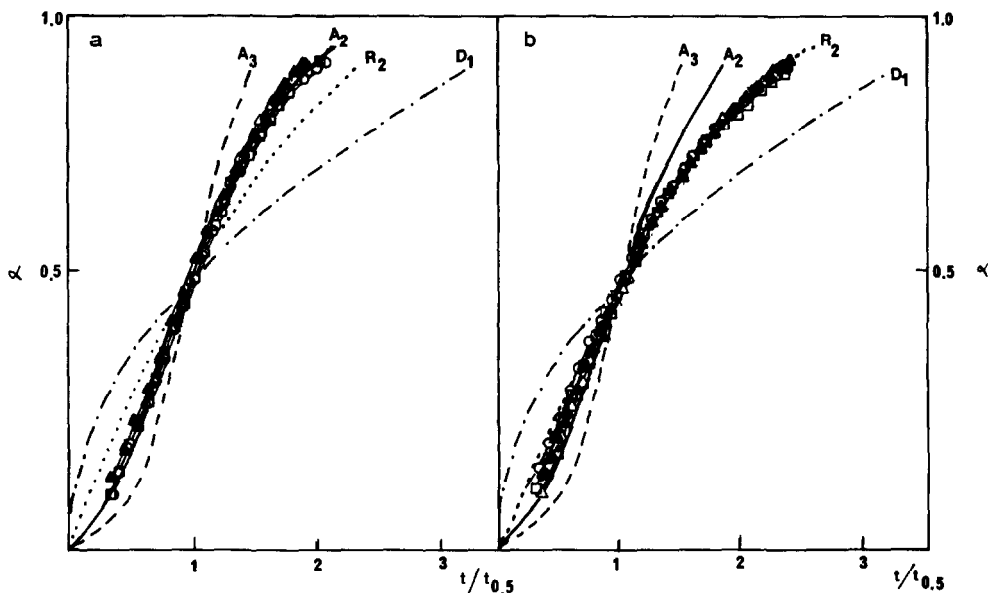| Mechanism	$g(\alpha)$
F$_1$ First order	$-\ln(1-\alpha)$
A$_2$ 2-D growth of nuclei	$(-\ln(1-\alpha))^{1/2}$
A$_3$ 3-D growth of nuclei	$(-\ln(1-\alpha))^{1/3}$
R$_2$ Contracting area	$1-(1-\alpha)^{1/2}$
R$_3$ Contracting volume	$1-(1-\alpha)^{1/3}$
D$_1$ 1-D diffusion	α^2
D$_2$ 2-D diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$
D$_3$ 3-D diffusion	$(1-(1-\alpha)^{1/3})^2$
D$_4$ Glinstling–Brounshtein	$(1-2\alpha/3)+(1-\alpha)^{2/3}$

Fig. 3. Reduced time plots for the isotherms of unground (a) and ground (b) β-PbO$_2$.

The isothermal data were analyzed using Avrami–Erofeev and interface advance mechanisms. The Arrhenius equation was applied to the values of k computed for these kinetic expressions and the activation energy values were calculated (see Table 3). It is worth noting that this parameter is practically independent of the kinetic law used in the study, as found in other kinetic analyses [9]. Thus, the operative kinetic law cannot be deduced by the analysis of these results.

The method of comparison of the kinetics of an isothermal solid-state reaction, based on the slope of the plot $\ln(-\ln(1-\alpha))$ vs. $\ln t$, was also applied to the data (Fig. 4). The mean value of the slope for the untreated sample was 1.717, which is closer to the theoretical value for A$_2$ mechanisms (2.00) than to any other law. In contrast, the mean value for ground β-PbO$_2$ was 1.329, closer to the expected value for a contracting area mechanism R$_2$

TABLE 3

Results of the application of the Arrhenius equation to the kinetic data for selected kinetic laws

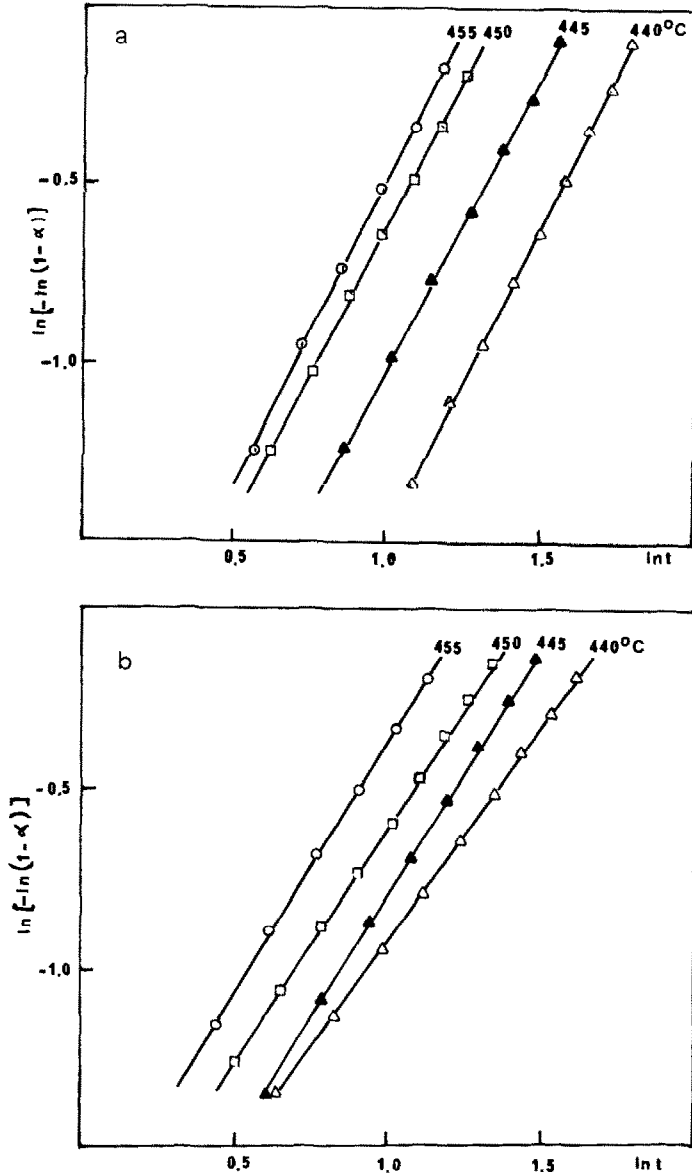| Kinetic expression	Unground β-PbO$_2$		Sample ground 300 min	
	r	E_a (kJ mol^{-1})	r	E_a (kJ mol^{-1})
A$_2$	0.960	143	0.980	157
A$_3$	0.955	139	0.991	160
R$_2$	0.966	144	0.984	157
R$_3$	0.969	146	0.984	157

Fig. 4. Plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ for unground (a) and ground (b) β-PbO_2.

(1.11). These results are in agreement with a careful examination of the reduced time plots in Fig. 3.

From the above results it can be deduced that the mechanochemical treatment of β-PbO_2 induces a change in the mechanism governing the phase transition from two-dimensional growth of nuclei to interface advance, probably following a contracting area model. This change is also accompanied by a slight increase in activation energy (Table 3). This

behaviour can be explained by considering the changes induced by the mechanical treatment if the results in Table 1 are taken into account. The initial Pb(II) content in lead dioxide samples has been shown to be accompanied by the presence of OH groups located at distorted zones of the solid [10]. This content increases with the mechanical activation of the samples [6]. The chemical reactions that take place on thermal treatment of PbO_2 begin with the release of these hydroxyls as water molecules plus a small amount of O_2, which is a starting point for further decomposition. When the phase transformation $\beta-\alpha$ is the only process, the O_2 release and Pb(II) increase are small (Table 1). However, these changes are necessary for the $\beta-\alpha$ conversion. Thus the above-mentioned distorted zones may be considered to be the initial nuclei of the transformation. For the unground β-PbO_2 the smaller amount of these nuclei may be responsible for the growth-of-nuclei controlled mechanism. As the number of initial nuclei increases with grinding, their growth is easily achieved and the advance of the resulting interface $\alpha-\beta$ is the rate-determining step of the reaction.

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