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EFFECT OF HEATING RATE ON THE THERMAL DECOMPOSITION OF LEAD DIOXIDE

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Experimental data are presented on the kinetics and mechanism of PbO_2 decomposition at heating rates varying from 0 to $2.5 \cdot 10^3$ °/sec. The studies were carried out with a time-of-flight mass spectrometer MSKH-4, a Paulik—Paulik—Erdey derivatograph and an X-ray diffractometer DRON-0.5

At low heating rates (0 to 0.2 °/s) oxygen is evolved in four stages: $PbO_2 \rightarrow PbO_{1.56} \rightarrow PbO_{1.44} \rightarrow PbO$. At extremely high heating rates ($2 \cdot 10^2 - 2.5 \cdot 10^3$ °/s) the number of stages is reduced to two: $PbO_2 \rightarrow PbO_{1.4} \rightarrow PbO$. An attempt is made to connect the observed change in the decomposition mechanism of PbO_2 with the crystal structure formation of the lead oxides.

Heating rate is one of the most important parameters affecting the course of chemical reactions. By changing heating rate over a wide range, reaction kinetics can substantially be changed, e.g. the stages controlling the overall rate of reaction may change [1], as was observed in particular for ammonium perchlorate [2].

In the present paper, results of a study on the thermal decomposition of lead dioxide are presented. Heating rate was varied over two widely different ranges:

(i) from 0 to 0.2° per second, and
(ii) from 200 to 2500° per second.

The choice of lead dioxide as object of the study and of the above heating rate ranges was motivated by the followings:

(i) We intended to study the mechanism of self-propagating reactions PbO_2 with such oxides as MoO_2 in cases where the heating rate in the reaction front is of the order of 1000°/sec.

(ii) Thermal decomposition of lead dioxide proceeds in distinct macrokinetic stages. (According to [3], PbO_2 loses oxygen – at decomposition conditions of slow heating – in four successive stages.)

(iii) It appeared of interest, in addition to obtain a first information on the effect of heating rate on the macrokinetic stages of the complex process, to compare the results obtained in usual standard apparatus for thermal analysis with the results of the impulse method allowing to study the course of the reaction directly at extremely high heating rates.

Experimental

For low heating rates (from 0.02 to 0.2°/s we used the Paulik – Paulik – Erdey derivatograph [4], a time of-flight mass spectrometer MSKH-4, and an X-ray diffractometer DRON-0.5 with a copper anode ($\lambda_{K\alpha}$ = 1.5418 Å).

For studies of the decomposition kinetics of PbO_2 at high heating rates (from 200 to 2500°/sec) we utilized the pulse mass spectrometer method corresponding to the recommendations in our earlier papers [1, 5]. The essential differences as compared to earlier apparatus described in [6, 7] were the use of the improved time-flying mass spectrometer MSKH-4 and of the high-speed camera Pentacet-35, allowing to film the screen of the electronic oscillograph with a speed of 400 shots per sec. (The Pentacet-35 camera is capable of taking 40,000 shots/sec.)

Experimental results

Low heating rates

Typical thermoanalytical curves obtained at heating rates of 0.02 – 0.2°/s or 1 and 10°/min, resp., are presented in Figs 1 and 2.

The main result is that in the investigated range, the four-stage decomposition of PbO_2 is retained. Details on the effect of heating rate may be seen in Table 1, where the temperature ranges for each of the four stages at different heating ranges are presented. For comparison, Otto's data [3] are also shown in the Table.

The data in the Table indicate that with increasing heating rate, the majority of the macrokinetic stages is shifted towards higher temperatures. Only the start of the fourth stage is shifted in the reverse sense. As a result, the time and temperature intervals, resp., between the 3rd and 4th stages decrease practically to zero. It may hence be assumed that a further increase in heating rate would result in the fusion of these two stages.

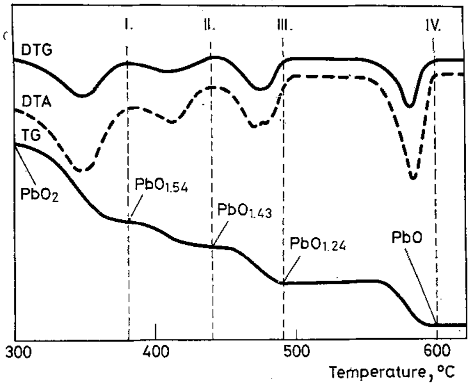

Fig. 1. Thermoanalytical curves of the thermal decomposition of PbO_2 at a heating rate of $2 \cdot 10^{-2}$ °/sec

No such express trend to fusion is observable with the other stages, as may be seen from the differences between the initial temperatures and the temperatures corresponding to maximum rates of reaction for the individual stages.

We attempted to determine the phase composition of the lead oxides for each stage. Diffraction patterns were taken at ambient temperature with the specimens having been subjected to heating, and also at high temperatures with one and the same specimen located in a high-temperature chamber, at successively raised temperatures. In the latter case the X-ray diffraction patterns were taken repeat-

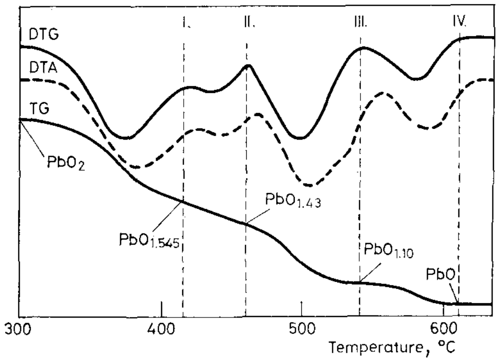

Fig. 2. Thermoanalytical curves of the thermal decomposition of PbO_2 at a heating rate of $3 \cdot 10^{-1}$ °/sec

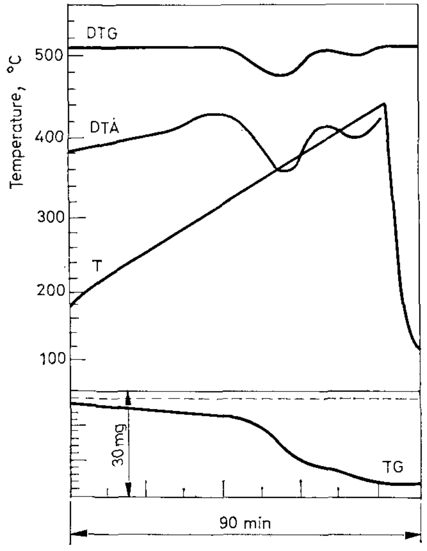

Fig. 3. Thermoanalytical curves obtained with the derivatograph in the course of preparing one of the specimens for X-ray phase analysis. G_0 = 500 mg

edly at a constant temperature as long as the intensity of the lines did not cease to change. The total time of keeping the specimen at each temperature varied from 40 minutes to 2 hours. In the case of preliminary heat treatment, the specimens were heated in the derivatograph at heating rates of 1 and 3°/min, resp., up to the temperatures corresponding to maximum rates of reaction, and to the final temperature of each stage. Simultaneously, the thermoanalytical curves were recorded. One set of these curves is shown in Fig. 3. The diffraction patterns of the starting material and of the products formed till the final moment of the stage in question are presented in Fig. 4.

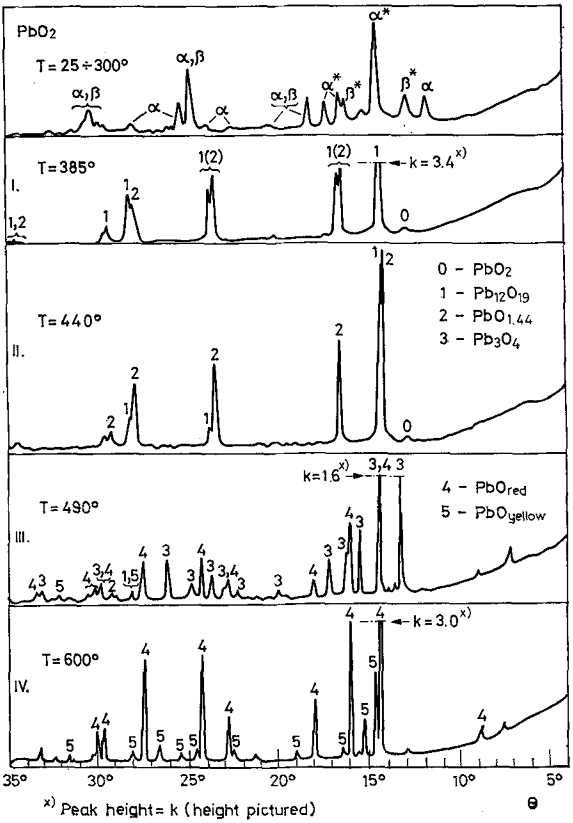

Fig. 4. Diffraction pattern of PbO_2 and its decomposition products after heating to the temperatures I, II, III and IV indicated in Figs 1 and 2

The analysis of the diffraction patterns and comparison with data in the literature [8] yielded the following results:

(i) The studied PbO_2 sample is a mixture of α and β modifications.

(ii) Changes in the intensity of the lines take place in the same temperature ranges where peaks are observed on the thermoanalytical curves.

Up to 280°, the phase composition of the initial PbO_2 does not change. A change begins at $T = 290-300°$, where the lines of PbO_2 begin to fade. Simultaneously, the first lines of the phases $Pb_{12}O_{19}$ and $PbO_{1\cdot 43}$ appear. It should be noted that it is very difficult to distinguish these phases, since their lines are extremely close. However, it is clearly manifested that these phases pass through a maximum at different temperatures: for $Pb_{12}O_{19}$ it is the final temperature of the first stage, i.e. 380–385°, while for $PbO_{1\cdot 43}$ it is the final temperature of the second stage, i.e. 440–450°. It should be noted that in the second case, the lines of Pb_3O_4 are still lacking. They appear only later, at $T \approx 470°$, simultaneously with the first appearance of PbO_{red} lines.

Like in the previous cases, intensity of Pb_3O_4 lines is maximum at the final temperature of the 3rd stage, i.e. at $T = 490°$ at a heating rate of 0.02°/sec. Maximum intensities of the lines of PbO_{red} were recorded at $T = 600°$. At this temperature, the high-temperature modification PbO_{yellow} is also present.

Thus, the sequence of phase formation, or rather the sequence of maximum intensity of their lines can be represented as follows:

$$PbO_2 \rightarrow PbO_{1\cdot 56} \rightarrow PbO_{1\cdot 43} \rightarrow PbO_{1\cdot 33} \rightarrow PbO_{red} \rightarrow PbO_{yellow}$$

High heating rates

Figs 5 and 6 represent the results of two typical mass spectrometer runs at heating rates of $2.1 \cdot 10^2$ and $2.5 \cdot 10^{3}$°/sec. resp. Similarly to low heating rates, the number of stages over this range of heating rates remained unchanged; however, instead of four stages of oxygen evolution, only two macrokinetic stages can be observed. The characteristics for each of these stages are presented in Table 2.

Table 2

Values of characteristic temperatures, indices x in the formula PbO_x, activation energies and pre-exponential factors, from mass spectrometric data

v, °/sec	x	Stage I				Stage II			
		T_{in}, °C	T_f, °C	E_I, kcal/mol	lg Z_I*	T_{in} °C	T_f °C	E_{II}, kcal/mole	lg Z_{II}*
$2.1 \cdot 10^2$	1.45±0.04	380	490	35±1	10.7±0.6	490	580	54±2	14.9±0.7
$2.5 \cdot 10^3$	1.40–1.35	450	580			580	700		

* $[Z_i]$ – sec^{-1}

The data indicate that the main effect of increasing heating rates consists in a noticeable shift of the stages towards higher temperatures (by 70 – 90°) and in an insignificant broadening of the temperature range over which the reaction takes place (by 20 – 30°). The oxygen content of the intermediate oxide remains practically unchanged and is equal to the value recorded in the final moment of the second stage in the low heating rate experiments. Hence one may presum-

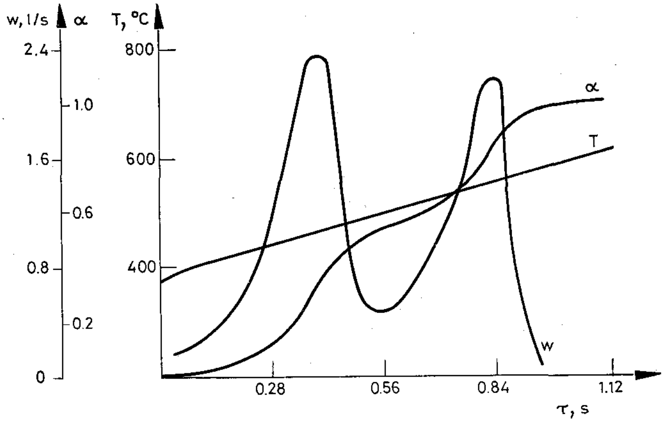

Fig. 5. Mass spectrometric data at a heating rate of $v = 2.1 \cdot 10^2$ °/sec; α = proportion of oxygen evolved according to the reaction $PbO_2 = 1/2O_2 + PbO$; $w = \frac{d\alpha}{dt}$; T = temperature

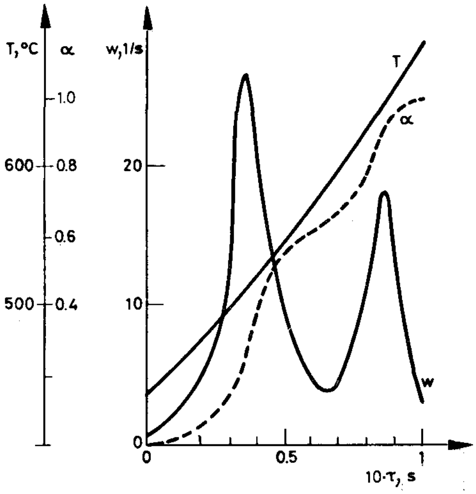

Fig. 6. Mass spectrometric data at a heating rate of $v = 2.5 \cdot 10^3$ °/sec

ably speak of fusion of the first stage with the second stage, and fusion of the third stage with the fourth stage. The latter was to be expected from the former experiments, while fusion of the first and second stages appears novel and unexpected.

Discussion

As indicated by X-ray phase analysis data, oxygen evolution is closely connected with the relationships governing crystal structure formation of the intermediate lead oxides. Thus, formation of the phase Pb_3O_4, when heating rate is increased, extends over an increasingly large temperature range up to the temperature at which intense formation of PbO_{red} starts (cf. Table 1), obviously owing to some particular delay in the formation of its crystalline structure. It may hence be assumed that at extremely high heating rates this structure will not succeed to form, and decomposition of the phase $PbO_{1\cdot 43}$ will directly lead to PbO.

In the case of the first and second stages, another mechanism of their fusion when changing over from low to extremely high heating rates appears more probable. Apparently the sequence of phase formation, namely first $Pb_{12}O_{19}$, then $PbO_{1\cdot 43}$ (according to Otto [3], $5PbO_2 \cdot 4PbO \rightarrow 4PbO_2 \cdot 5PbO$) is retained. However, the formation of the second phase is a faster process (let us remind that its first lines appear practically simultaneously with the lines of $Pb_{12}O_{19}$). As a result, for a short period a quasi-steady state will be established, in which the amount of the phase $Pb_{12}O_{19}$ is very small, and the two subsequent macrokinetic stages degenerate into one recorded stage.

The fact that activation energy values calculated by Satava's method [9] for the first stage at both investigated heating rates are identical ($E = 35$ kcal/mole) speaks in favour of this explanation.

In conclusion, we wish to note that the present investigation again proves, first, the importance of the parameter heating rate in kinetic studies of solid-phase chemical reactions using non-isothermal methods, and second, the impossibility, in the general case, to reliably extrapolate results obtained at low heating rates to extremely high heating rates. The data also demonstrate that the key to an understanding of the macrokinetics of PbO_2 decomposition consists in elaborate studies on the kinetics of formation of the intermediate phases.

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Résumé — On présente des résultats expérimentaux concernant la cinétique et le mécanisme de la décomposition de PbO_2 pour des vitesses de chauffage allant de 0 à $2.5 \cdot 10^{3\circ}/s$. Les études ont été effectuées à l'aide d'un spectromètre de masse du type MSKH-4, d'un Dérivatograph du type Paulik—Paulik—Erdey et d'un diffractomètre des rayons X du type DRON—0,5.

Aux faibles vitesses de chauffage (0 à 0.2°/s) l'oxygène se dégage en quatre étapes: $PbO_2 \rightarrow PbO_{1.56} \rightarrow PbO_{1.44} \rightarrow PbO$. Aux vitesses de chauffage très élevées ($2 \cdot 10^2$ à $2.5 \cdot 10^{3\circ}/s$) le nombre des étapes se réduit à deux: $PbO_2 \rightarrow PbO_{1.4} \rightarrow PbO$. On essaye de relier le changement observé dans le mécanisme de décomposition de PbO_2 à la structure cristalline des oxydes de plomb.

Zusammenfassung. — Versuchsergebnisse bezüglich der Kinetik und des Mechanismus der Zersetzung von PbO_2 bei Aufheizgeschwindigkeiten zwischen 0 und $2.5 \cdot 10^3$ °/s werden mitgeteilt. Die Untersuchungen wurden mittels eines "time-of-flight" Massenspektrometers MSKH-4, eines Derivatographen des Typs Paulik—Paulik—Erdey und eines Röntgendiffraktometers DRON—0.5 durchgeführt.

Bei niedrigen Aufheizgeschwindigkeiten (0 bis 0.2 °/sec) wird Sauerstoff in vier Stufen entwickelt: $PbO_2 \rightarrow PbO_{1.56} \rightarrow PbO_{1.44} \rightarrow PbO$. Bei extrem hohen Aufheizgeschwindigkeiten ($2 \cdot 10^2 - 2.5 \cdot 10^3$ °/s) wird die Zahl der Stufen auf zwei herabgesetzt: $PbO_2 \rightarrow PbO_{1.4} \rightarrow$ $\rightarrow PbO$. Es wird versucht die beobachtete Änderung in dem Zersetzungsmechanismus von PbO_2 mit der Kristallstrukturbildung der Bleioxide in Verbindung zu bringen.

Резюме — Представлены экспериментальные результаты по кинетике и механизму разложения PbO_2 при варьировании скоростей нагревания от 0до $2.5 \cdot 10^3$ °/с. Изучение проведено с использованием время — пролетного масс — спектрометра МСХ — 4, дериватографа системы Паулик—Паулик—Эрдеи и рентгеновского дифрактометра ДРОН — 0.5.

При низких скоростях нагрева (0—0.2°/с) кислород выделяется в четыре стадии: $PbO_2 \rightarrow PbO_{1.56}$. → .$PbO_{1,44} \rightarrow PbO$. При экстремально высоких скоростях нагревания ($2 \cdot 10^2$—$2.5 \cdot 10^3$ °/с) число стадий сокращается до двух: $PbO_2 \rightarrow PbO_{1.4} \rightarrow PbO$. Сделана попытка связать наблюдающиеся исменения механизма термического разложения PbO_2 с перестройкой кристаллической структуры окислов свинца.

Table 1

Values of the characteristic temperatures[1] and x_i indices in the formula PbO_{x_i} for the four stages of PbO_2 decomposition, from DTG and X-ray phase analysis data

Heating rate, °/min	1st stage					2nd stage					3rd stage						4th stage					T_{max}[3]		
	T_{in}	T_{max}	T_f	x	T_f-T_{in}	T_{in}	T_{max}	T_f	x	T_f-T_{in}	T_{in}	T_{max}	T_f	x	T_f-T_{in}	$T_{in_i}-T_{f_i}$[2]	T_{in}	T_{max}	T_f	x_i	T_f-T_{in}	2–1	3–2	4–3
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
0*	260	260	260	1.56	0	325	325	325	1.44	0	350	350	350	1.33	0	185	535	535	535	1.00	0	65	25	185
0[4]	290–300	350–370	(390?)	1.58 (1.54)	(90–100?)	(390?)	390–420	(420?)	1.5(?)	(30?)	430	430–440	440	1.33	10?	130	570	570–580	580	1.00	10(?)	20–70?	10–50(?)	130–150(?)
?**	330	(345)	360	1.56	30	360	(390)	420	1.44	60	450	(455)	460	1.33	10	105	565	570	575	1.00	10	(45)	(60)	(115)
1	300	350	380	1.545	80	380	410	440	1.43	60	440	470–475	490	1.24	50	60	550	580	595	1.00	45	60	60–65	105–110
3	300	365	400	1.54	100	400	425	450	1.42	50	450	485	510	1.15	60	40	550	585	600	1.00	50	60	60	100
5	300	360	395	1.565	95	395	420	440	1.43	45	440	485	510	1.05	70	30	540	565	585	1.00	45	60	65	80
10	310	375	415	1.545	105	415	435	455–460	1.43	40–45	455–460	495	540	1.10	80–85	0	540	580–585	610	1.00	65	60	60	85–90

[1] All temperatures in °C

[2] In all other cases the intervals between stages were equal to zero

[3] Temperature differences between the maxima of neighbouring peaks

[4] Data obtained by X-ray phase analysis

* Phase transition temperatures at equilibrium conditions in air (pressure of oxygen – 0.21 atm) according to Otto's data [3]

** Results obtained by Otto [3] at slow heating