*Thermochimica Acta*, 107 (1986) 305–319
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# SOLID STATE PREPARATIVE AND DESCRIPTIVE THERMOANALYSIS OF $SnO_2$–$X_2S_2O_8$ AND $PbO_2$–$X_2S_2O_8$ (X = Na, K) BINARY SYSTEMS

HADI. H. JASIM and FADHIL JASIM *

*Department of Chemistry, College of Sciences, University of Baghdad, Jadiriya, Baghdad (Iraq)*

(Received 14 April 1986)

## ABSTRACT

Thermoanalysis of two congener oxides of group IV, $SnO_2$ and $PbO_2$, alone or in binary mixtures with either $Na_2S_2O_8$ or $K_2S_2O_8$, using the derivatograph is described. The results have shown that either oxide could catalytically lower the $T_i$ of decomposition of the peroxosalt–pyrosulphate transformation by about 10–20°C. Similarly lowered was the $T_i$ of degradation of $X_2S_2O_7$. $SnO_2$ was found to react in the solid state with $X_2S_2O_7$ to form the mixed oxides $Na_2Sn_2O_5$ and $K_2Sn_3O_7$; the stoichiometric equations, range of thermal stabilities and melting points have been assigned. An intermediate, $Na_2Sn_2O(SO_4)_2$, was anticipated. Both mixed oxides were white crystalline powders. $PbO_2$ forms double salts with $X_2S_2O_7$ ($Na_2Pb(SO_4)_2$ and $K_2Pb(SO_4)_2$) whose thermal stabilities, melting points, phase change and XRD patterns were assigned. A melting eutectic consisting of ($Na_2Pb(SO_4)_2$ + PbO) was identified. X-ray diffraction was used as a complementary analytical tool for identifying intermediate and final products.

## INTRODUCTION

The white tetragonal $SnO_2$ crystal is an n-type semiconductor whose melting and boiling points are approximately 1898 and 2000°C, respectively. At about 683°C $\alpha$-$SnO_2$ is converted into the $\beta$-form. $PbO_2$ has two crystalline phases; $\alpha$-$PbO_2$ is rhombic whereas the $\beta$-phase is tetragonal. The latter has the greater specific conductance; $10^4$ $ohm^{-1}$ $cm^{-1}$ and $10^3$ $ohm^{-1}$ $cm^{-1}$, respectively. $PbO_2$ is an n-type semiconductor with an m.p. of 290°C. The active materials of the positive plate of accumulators consist mainly of $PbO_2$ which is present in $\alpha$- and $\beta$-phases; the latter is preferable for improved electrical conductance. The decomposition of $\alpha$- and $\beta$-phases differs since each has different properties. In an $\alpha$–$\beta$ mixture, the $\alpha$-phase starts decomposing first, followed by the $\beta$-phase, producing first $Pb_3O_4$ and eventually PbO. The decomposition of $\beta$-$PbO_2$ leads to the formation of

---

* To whom correspondence should be addressed.

0040-6031/86/$03.50

$PbO_x$ ($x = 1.58$ and 1.46) then $Pb_3O_4$ (red-orange) and finally $\beta$-PbO (yellow); $\alpha$-$PbO_2$ does not form $Pb_3O_4$ but converts directly into $\alpha$-PbO (red) [1,2]. Other workers claimed, through their TG investigations, the formation of the intermediate $Pb_2O_3$ before the $Pb_3O_4$ step. The latter, decomposes between 552 and 660°C whereas the former is stable between 375 and 460°C.

Both tin and lead are amphoteric ions which react in solution with, say, sulphates or sulphites to form the corresponding insoluble salts. The rutile structure of $Sn(SO_4)_2$ differs from the hexagonal $Sn(SO_4)_2 \cdot 2\ H_2O$ which loses its water of hydration between 150 and 260°C [3]. Many sulphates and double salts of lead have been prepared in solution [5–7], but almost no procedures have been described for their preparation via solid state reactions. The aim of this paper is to investigate the high temperature, solid state reactions of $SnO_2$ and $PbO_2$ alone and in binary systems with the peroxodisulphates of Na and K, leading to the preparation and description of their sulphates, double salts, mixed oxides and the disclosure of their catalytic activity towards the thermolysis of pure alkali persulphates.

## EXPERIMENTAL

All chemicals used were of analytical reagent grade; $SnO_2$ and $PbO_2$ from Fluka AG, Buchs SG, $Na_2S_2O_8$ and $K_2S_2O_8$ from BDH. $\alpha$-$Al_2O_3$ from MOM, sintered at 1300°C was used as a reference material.

Apparatus, technique and thermoanalysis procedures were as described elsewhere [4].

## RESULTS AND DISCUSSION

### *Thermoanalysis of $SnO_2$ and $PbO_2$*

The TG, DTG and DTA curves (Fig. 1) infer that $SnO_2$ remains thermally stable to the end of the heating programme (1050°C) except for a loss of 12 wt.% perhaps due to escape of a volatile impurity originally present in the reagent. The XRD patterns of the final products confirm that only $SnO_2$ is present. Some workers claimed that $SnO_2$ undergoes an $\alpha$- to $\beta$-modification around 683°C [8]. However, this phase change is not seen on the DTA curve of Fig. 1; may be due to the low sensitivity used in the analysis or the rate of heating being too low to sense the small change in sample and reference thermocouples.

Figure 2 depicts the derivatograms of pure $PbO_2$ which show that it is thermally stable up to 380°C. The two overlapping endotherms on the TG curve indicate two decomposition stages between 380 and 520°C. Mass

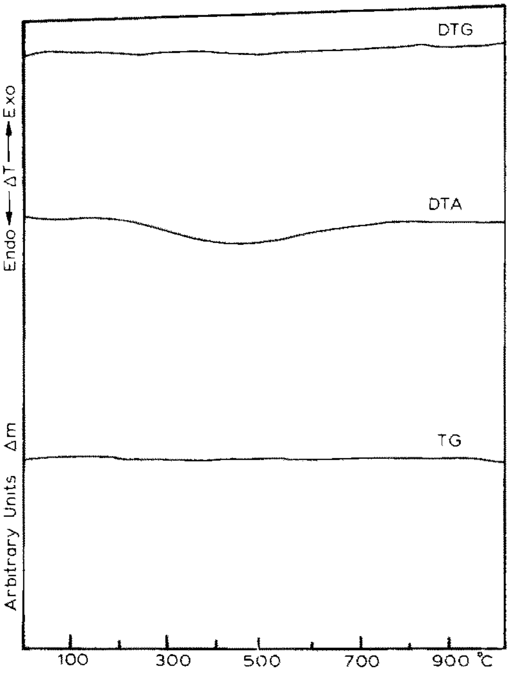

Fig. 1. Thermogram of tin(IV) oxide, $SnO_2$.

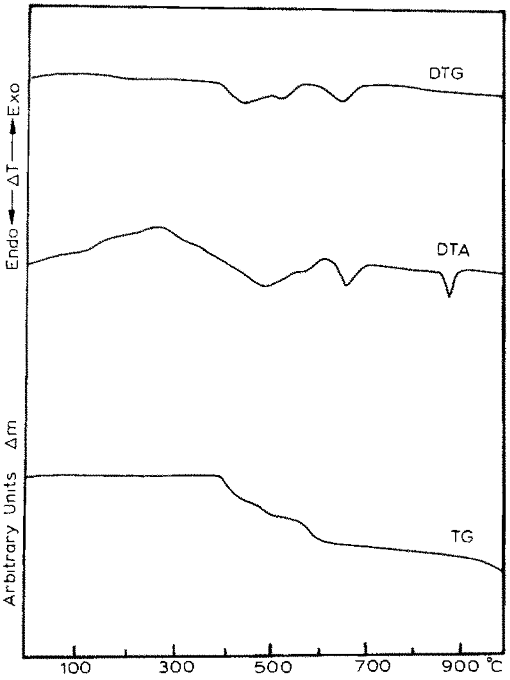

Fig. 2. Thermogram of lead(IV) oxide, $PbO_2$.

losses of 3.25 and 1.30 wt.% occur at 380–470 and 470–520°C resulting in the formation of defective or non-stoichiometric $\beta$-$PbO_x$ oxides. The XRD patterns for specimens heated up to 470°C confirm the presence of $\alpha$-$PbO_{1.55}$ and $\beta$-$PbO_{1.44}$ [9,10], whereas those isolated at 540°C confirm the presence of red lead, $PbO_{1.333}$ or $Pb_3O_4$ [11]. Surprisingly no peak belonging to $Pb_2O_3$ could be detected on the TG and DTG curves of Fig. 2, probably due to low TG (200 mg), DTG (1/10) or DTA sensitivities of the instrument. Between 500 and 620°C $Pb_3O_4$ gradually decomposes with an overall mass loss of 2 wt.%. Thereafter the TG curve remains relatively thermally stable up to 920°C due to the formation of PbO. The typical sharp melting endotherm of yellow PbO appears at 885°C [12]. Since the lead oxides are thermally unstable, therefore none of them could be recommended as a gravimetric residue.

It was concluded that $SnO_2$ is thermally more stable than $PbO_2$. This is because the divalent state of $Pb^{2+}$ is more stable than the tetravalent one (Pb has a higher atomic number); therefore, $PbO_2$ is a more powerful oxidising agent than $SnO_2$ and as such it has a greater tendency to form ionic compounds such as double salts of sulphates or phosphates than Sn.

### *Thermoanalysis of the $SnO_2$–$Na_2S_2O_8$ system*

Figure 3 exhibits the TG and DTA (DTG is not shown for the sake of space saving) curves for the various molar ratios of this system from ambient to 1050°C. The $T_i$ of $Na_2S_2O_8$ decomposition is catalytically lowered by 10°C for the ratios 1 : 4 and 1 : 2, by 15°C for the ratio 1 : 1, and by 20°C for 2 : 1 and 4 : 1. Thus, it could be concluded that the lowering increases with $SnO_2$ concentration. Also $SnO_2$ has catalytically lowered the m.p. of $Na_2S_2O_7$ and this lowering depends upon the $SnO_2$–$Na_2S_2O_8$ ratio (Table 1); for the ratios 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 1 : 4, it is, respectively, 5, 10, 20, 20 and 20°C. As the TG curves reveal, the decomposition of $Na_2S_2O_7$ takes place in three instead of two steps in the 1 : 2 mixtures. Moreover, small exotherms are observed on the DTA curves: 1 : 4, 1 : 2, 1 : 1 and 2 : 1. The last one is the sharpest which represents an exothermic reaction between $SnO_2$ and $Na_2S_2O_7$ at 500, 540 and 550°C, respectively. Since this is accompanied by a gradual mass loss, as the corresponding TG curves indicate, it is expected that an unstable intermediate compound is formed. Samples heated to 580 and 800°C for the ratio 2 : 1 give XRD patterns for the mixed oxide $Na_2Sn_2O_5$ and for $Na_2SO_4$ (Table 2) which are similar to other research results [13]. Samples heated to 1000°C for the ratios 1 : 1 and 2 : 1 give similar XRD patterns which indicates that the mixed oxide $Na_2Sn_3O_5$ is stable even beyond the ceiling temperature of the heating programme. Computation from TG curves for the 2 : 1 mixture (Table 1) inform that 51.09 wt.% of $Na_2S_2O_7$ reacts with the available $SnO_2$; from

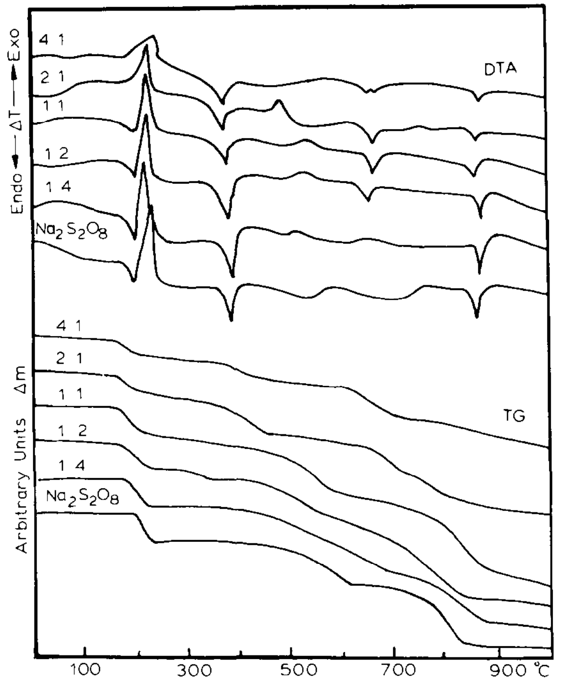

Fig. 3. TG and DTA curves of tin(IV) oxide–sodium persulphate mixture.

which it can be concluded that 2 : 1 :: $SnO_2 : Na_2S_2O_8$ is the stoichiometric ratio; the stoichiometric reaction can be written as

$$Na_2S_2O_7 + SnO_2 \xrightarrow{\Delta} Na_2Sn_2O_5 + 2\ SO_3$$

It is to be observed that the sharpest exotherm and XRD lines appear in the 2 : 1 mixture only among all other ratios of this system.

The small sharp endotherms that appear at about 685 °C for the ratios 1 : 2, 1 : 1 and 2 : 1 belong to $\alpha$- and $\beta$-modifications, probably of the mixed oxide (since the $\alpha$- to $\beta$-modification of $SnO_2$ is not shown on the DTA curve of Fig. 1).

The small pair of endotherms that appear on the DTA curve of the 4 : 1 mixture represents the $\alpha$ to $\beta$ change of the mixed oxide and its melting, respectively. The typical melting endotherm of $Na_2SO_4$ is shifted to lower values (865–885 °C). The small blunt exo-peak appearing in the 2 : 1 mixture at 775 °C is thought to pertain to the side reaction

$$Na_2S_2O_7 + 2\ SnO_2 \xrightarrow{\Delta} Na_2Sn_2O(SO_4)_2 + O_2 + \text{heat}$$

The small mass loss at this temperature seen on the TG curve is presumably due to the liberation of $O_2$, as a secondary reaction. XRD patterns for

TABLE 1

Preparation of standard molar ratios and TG results of the $SnO_2-Na_2S_2O_8$ system

| Mole ratio | $SnO_2$ (mg) | $Na_2S_2O_8$ (mg) | $O_2$ lost from $Na_2S_2O_2$ decomp. |  |  |  | $SO_3$ lost from $Na_2S_2O_7$ (mg) |  | m.p. of $Na_2S_2O_7$ | $Na_2S_2O_7$ react. (%) |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Mass (mg) |  | Temp. (°C) |  |  |  |  |  |
|  |  |  | Theor. | Pract. | $T_i$ | $T_f$ | Theor. | Pract. |  |  |
| 1:4 | 27.3 | 172.7 | 11.6 | 11.5 | 175 | 230 | 58 | 39 | 380 | 32.74 |
| 1:2 | 62.33 | 137.67 | 9.2 | 9.2 | 175 | 230 | 46.3 | 39 | 375 | 28.69 |
| 1:1 | 77.52 | 122.48 | 8.2 | 7.8 | 170 | 240 | 41.15 | 27 | 375 | 39.26 |
| 2:1 | 111.73 | 88.27 | 5.93 | 5.9 | 165 | 235 | 29.65 | 14.5 | 370 | 51.08 |
| 4:1 | 143.37 | 56.63 | 3.8 | 3.8 | 165 | 235 | 19 | 12 | 370 | 36.79 |

TABLE 2

XRD patterns for the prepared by-products $Na_2Sn_2O_5$ and $SnO_2$

| No. | $Na_2Sn_2O_5$ |  | $SnO_2$ |  |
|---|---|---|---|---|
|  | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ |
| 1 | 4.74 | 60 | 3.38 | 100 |
| 2 | 2.80 | 100 | 2.67 | 80 |
| 3 | 2.33 | 10 | 2.39 | 25 |
| 4 | 1.87 | 20 | 1.77 | 65 |
| 5 | 1.60 | 40 | 1.68 | 18 |
| 6 | 1.50 | 20 | 1.44 | 18 |
| 7 | 1.34 | 100 | 1.42 | 16 |

samples in this region reveal the presence of the mixed oxide but not $Na_2Sn_2O(SO_4)_2$, which suggests the transient nature of the latter:

$$Na_2Sn_2O(SO_4)_2 \xrightarrow{\Delta} Na_2Sn_2O_5 + SO_2$$

### *Thermoanalysis of the $SnO_2$–$K_2S_2O_8$ system*

Figure 4 depicts the TG and DTA curves of the various ratios. $T_i$ of the $K_2S_2O_8 \xrightarrow{\Delta} K_2S_2O_7$ transformation is catalytically lowered by about 15°C. Similarly, the $\alpha$- to $\beta$-phase transition of $K_2S_2O_7$ is lowered by about 20°C. The small wide exotherm at 390°C constitutes the excess heat energy that remains after thermal neutralisation with the phase transition endotherm, and in the meantime manifests the reaction between $SnO_2$ and $K_2S_2O_7$ which becomes more pronounced at ratios of 2 : 1 and 4 : 1, although it is shifted to temperatures lower than 390°C by the catalytic effect which increases with increasing $SnO_2$. Samples heated to 390°C give XRD patterns pertaining to the presence of the mixed oxide, $K_2Sn_3O_7$ (Table 4) [14] and $K_2S_2O_7$ [15]. Table 3 indicates that in the 2 : 1 mixture about 71.89 wt.% of $K_2S_2O_7$ reacts with the available $SnO_2$. This of course points out the stoichiometry of the reaction since it is the highest percentage of all ratios investigated. The XRD patterns of the final products confirm the presence of $K_2Sn_3O_7$, $SnO_2$ [16] and $\alpha$-$K_2SO_4$ [17]. The stoichiometric equation

$$K_2S_2O_7 + 3\ SnO_2 \xrightarrow{\Delta} K_2Sn_3O_7 + 2\ SO_3$$

suggests that the 1 : 3 mixture could be the alternative stoichiometric ratio. No explanation could be offered for this controversy.

### *Thermoanalysis of the $PbO_2$–$Na_2S_2O_8$ system*

Scrutiny of TG and DTA curves (Fig. 5) and data of Table 5 point out that $PbO_2$ could catalytically lower the $T_i$ of decomposition of $Na_2S_2O_8$ and

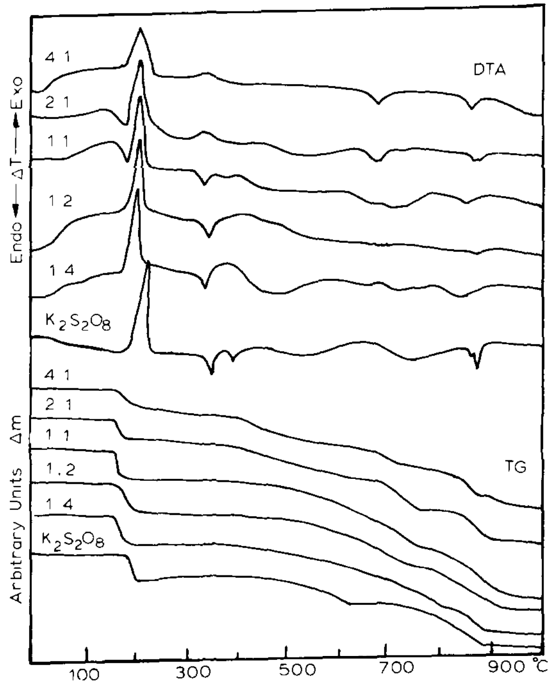

Fig. 4. TG and DTA curves of tin(IV) oxide–potassium persulphate mixture.

the lowering is proportional to the amounts of oxide present; it is 10, 15, 30, 30 and 30 °C for the ratios 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 4 : 1, respectively. $T_f$ does not change but remains the same as for the pure salt. The m.p. of $Na_2S_2O_7$ is also catalytically lowered from 380 to 350 and 370 °C for 1 : 4 and 1 : 2, respectively. For other ratios the melting endotherm of $Na_2S_2O_7$ vanishes since it is all consumed through the solid–solid $PbO_2$–$Na_2S_2O_7$ reaction before melting. The relatively small exo-peaks appearing between 260 and 300 °C in the ratios 1 : 2, 1 : 1, 2 : 1 and 4 : 1 indicate an exothermic solid–solid reaction between $PbO_2$ and $K_2S_2O_7$. The exo-peak is not very clear in the 1 : 4 mixture owing to a negligible extent of reaction. In the 1 : 1 mixture the exo-peak is of maximum area (270 °C) which supports a stoichiometric reaction of the type

$$Na_2S_2O_7 + PbO_2 \xrightarrow{\Delta} Na_2Pb(SO_4)_2 + {}^{1}\!/_{2}\, O_2$$

Samples heated to 400 °C give XRD patterns that are in part identical with those belonging to $PbO_2$ (excess) and in part to an unknown phase (Table 5). Since the plateau remains stable over the entire range (340–900 °C) on the TG curve this means that the prepared double salt is also stable. Proofs for the stoichiometric 1 : 1 ratio are multiple: the disappearance of the $Na_2SO_4$ endotherm, the similar values of theoretical (3.30%) and experimen-

TABLE 3

Preparation of standard molar ratios and TG results of the $SnO_2$–$K_2S_2O_8$ system

| Mole ratio | $SnO_2$ (mg) | $K_2S_2O_8$ (mg) | $O_2$ lost from $K_2S_2O_8$ decomp. |  |  |  | $SO_3$ lost from $K_2S_2O_7$ decomp. (mg) |  | m.p. of $K_2S_2O_7$ | $K_2S_2O_7$ react. (%) |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Mass (mg) |  | Temp. (°C) |  |  |  |  |  |
|  |  |  | Theor. | Pract. | $T_i$ | $T_f$ | Theor. | Pract. |  |  |
| 1:4 | 24.5 | 175.5 | 10.3 | 10.2 | 165 | 200 | 51.93 | 28 | – | 46.07 |
| 1:2 | 43.6 | 156.4 | 9.2 | 9.1 | 165 | 200 | 46.2 | 23.5 | – | 47.8 |
| 1:1 | 71.6 | 128.4 | 7.6 | 7.7 | 165 | 200 | 38 | 16 | – | 57.89 |
| 2:1 | 105.5 | 94.5 | 5.59 | 5.4 | 165 | 200 | 27.96 | 87.8 | – | 71.89 |
| 4:1 | 138.08 | 61.92 | 3.66 | 3.6 | 165 | 200 | 18.32 | 10 | – | 45.4 |

TABLE 4

XRD patterns for the prepared by-product $K_2Sn_3O_7$

| No. | $K_2Sn_3O_7$ | |
|---|---|---|
| | $d$ (Å) | $I/I_0$ |
| 1 | 4.14 | 25 |
| 2 | 3.16 | 20 |
| 3 | 2.98 | 100 |
| 4 | 2.50 | 30 |
| 5 | 2.29 | 30 |
| 6 | 2.20 | 25 |
| 7 | 1.88 | 20 |
| 8 | 1.58 | 25 |
| 9 | 1.56 | 25 |
| 10 | 1.42 | 30 |

tally found (3.25%) oxygen; tetravalent $Pb^{4+}$ is less stable [18] than Pb(II); the majority of alkali metal elements form stable double salts which are usually prepared in solution [4–6]. The sharp endo-peaks appearing at different temperatures for the curves of ratios 1 : 2, 1 : 1, 2 : 1 and 4 : 1

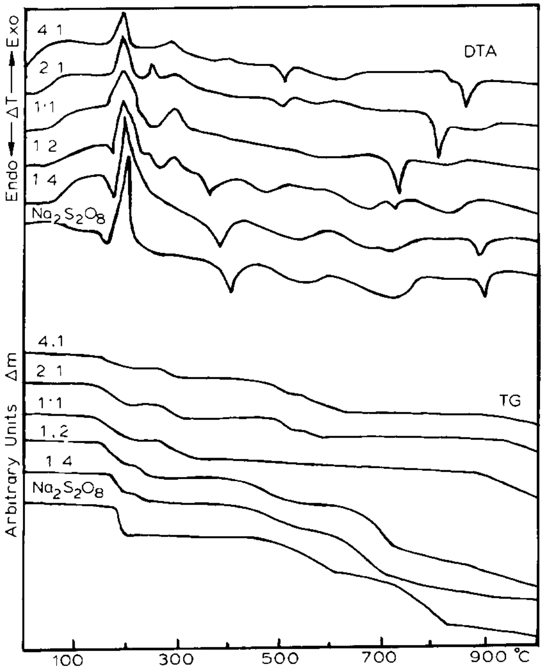

Fig. 5. TG and DTA curves of lead(IV) oxide–sodium persulphate mixture.

TABLE 5

Preparation of standard molar ratios and TG results of the $PbO_2$–$Na_2S_2O_8$ system

| Mole ratio | $PbO_2$ in sample (mg) | $Na_2S_2O_8$ in sample (mg) | $O_2$ lost from $Na_2S_2O_8$ decomp. | | | | $SO_3$ lost from $Na_2S_2O_7$ decomp. (mg) | | m.p. of $Na_2S_2O_7$ | $Na_2S_2O_7$ react. (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mass (mg) | | Temp. (°C) | | | | | |
| | | | Theor. | Pract. | $T_i$ | $T_f$ | Theor. | Pract. | | |
| 1:4 | 40.15 | 159.85 | 10.74 | 10.69 | 170 | 230 | 53.7 | 33 | 370 | 34.8 |
| 1:2 | 66.85 | 133.15 | 8.9 | 8.7 | 165 | 230 | 44.7 | 18 | 350 | 59.7 |
| 1:1 | 100.24 | 99.76 | 6.7 | 7 | 150 | 230 | 33.5 | 0 | – | 99.94 |
| 2:1 | 133.54 | 66.46 | 4.46 | 4.5 | 150 | 230 | 22.3 | 5 | – | 77.5 |
| 4:1 | 160.15 | 39.85 | 2.6 | 2.6 | 150 | 230 | 13.38 | 3.5 | – | 73.4 |

TABLE 6

XRD patterns for the by-products $Na_2Pb(SO_4)_2$, $Na_2SO_4$ and $PbSO_4$

| No. | $Na_2Pb(SO_4)_2$ | | $Na_2SO_4$ | | $PbSO_4$ | |
|---|---|---|---|---|---|---|
| | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ |
| 1 | 3.32 | 100 | 2.73 | 100 | 3.01 | 100 |
| 2 | 3.88 | 25 | 4.62 | 25 | 4.26 | 87 |
| 3 | 3.60 | 35 | 3.31 | 55 | 3.80 | 55 |
| 4 | 2.82 | 40 | 3.06 | 50 | 3.46 | 33 |
| 5 | 2.35 | 30 | 2.69 | 50 | 2.76 | 40 |
| 6 | 2.06 | 90 | 2.32 | 20 | 2.64 | 45 |
| 7 | 1.96 | 40 | 1.86 | 30 | 2.16 | 28 |
| 8 | 1.79 | 30 | 1.68 | 12 | 2.02 | 50 |

actually belong to $Na_2Pb(SO_4)_2$. Experiments have shown that the latter starts decomposition around 900°C.

$$Na_2Pb(SO_4)_2 \xrightarrow{\Delta} Na_2SO_4 + PbSO_4$$

X-ray diffraction of the final products confirms the presence of $Na_2Pb(SO_4)_2$, $Na_2SO_4$ and $PbSO_4$ (Table 6). The small endopeak appear-

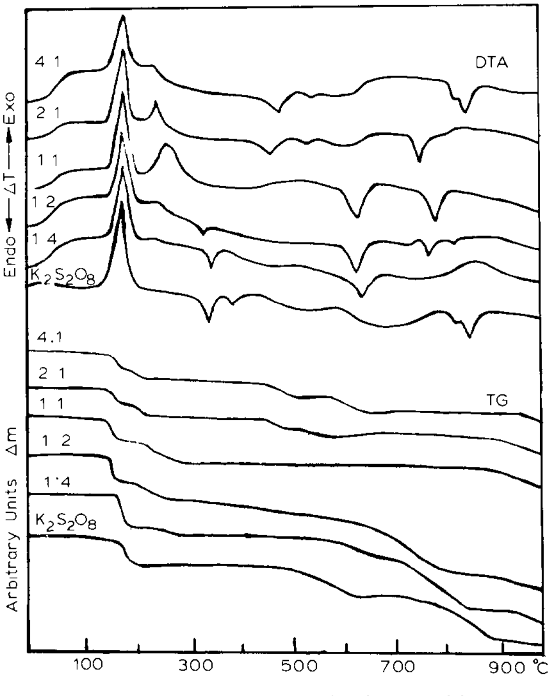

Fig. 6. TG and DTA curves of lead(IV) oxide–potassium persulphate mixture.

TABLE 7

Preparation of standard molar ratios and TG results of the $PbO_2$–$K_2S_2O_8$ system

| Mole ratio | $PbO_2$ in sample (mg) | $K_2S_2O_8$ in sample (mg) | $O_2$ lost from $K_2S_2O_8$ decomp. | | | | $SO_3$ lost from $K_2S_2O_8$ decomp. (mg) | | m.p. of $K_2S_2O_7$ | $K_2S_2O_7$ react. (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mass (mg) | | Temp. (°C) | | | | | |
| | | | Theor. | Pract. | $T_i$ | $T_f$ | Theor. | Pract. | | |
| 1:4 | 36.3 | 163.7 | 9.6 | 9.5 | 170 | 200 | 48.46 | 28 | – | 42.16 |
| 1:2 | 61.35 | 138.65 | 8.2 | 8.1 | 160 | 200 | 38.6 | 17 | – | 52.6 |
| 1:1 | 93.9 | 106.10 | 6.28 | 6.3 | 160 | 200 | 31.4 | 0 | – | 99.99 |
| 2:1 | 72.19 | 127.81 | 4.27 | 4.2 | 160 | 200 | 21.36 | 2 | – | 90.6 |
| 4:1 | 44 | 156 | 2.6 | 2.5 | 160 | 200 | 13.02 | 3 | – | 76.93 |

ing on the curve of 1 : 2 ratio belongs to the melting eutectic ($Na_2Pb(SO_4)_2$ + PbO).

*Thermoanalysis of the $PbO_2$–$K_2S_2O_8$ system*

The role of $PbO_2$ as a catalyst lowering $T_i$ for the $K_2S_2O_8 \rightarrow K_2S_2O_7$ reaction is clear from the TG and DTA curves of Fig. 6 and from data in Table 7. It is 10°C for 1 : 4, and 20°C for other ratios. $T_i$ of the $\alpha$- to $\beta$-phase change of $K_2S_2O_7$ is lowered by 10°C in ratio 1 : 2; for other ratios the phase change disappears due to complete interaction of $K_2S_2O_7$. The exo-peaks, appearing between 200 and 300°C, that belong to 1 : 1, reach a maximum. Samples heated immediately after this exo-peak (350°C) yield patterns typical of $PbO_2$, $K_2S_2O_7$ and $K_2Pb(SO_4)_2$ [11} (Table 7). The mass loss on the TG curve at this temperature is ascribed to the liberation of $O_2$. Table 7 indicates that 99.99 wt.% of $K_2S_2O_7$ reacts with the available $PbO_2$ in the ratio 1 : 1; therefore, the stoichiometric reaction can be written as

$$K_2S_2O_7 + PbO_2 \xrightarrow{\Delta} K_2Pb(SO_4)_2 + {}^{1/2}\, O_2$$

The crystalline phase-change endotherm of this double salt is observed on the DTA curves of the 4 : 1, 2 : 1 and 1 : 1 mixtures. This is confirmed by heating two samples of ratio 1 : 1 before and after the endotherms at 520 and 690°C, respectively. The X-ray analyses for either powders obtained infer the existence of $PbO_{1.44}$, $PbO_{1.55}$ and $K_2Pb(SO_4)_2$ (Table 8).

The sharp endotherms observed at 740, 780 and 770°C for the ratios 1 : 2, 1 : 1 and 2 : 1, respectively, belong to the melting of the double salt. This is confirmed by heating 1 : 1 samples to 820°C, after which a yellowish melt was found. Naturally, the variation of melting temperature is due to the variation of $PbO_x$ content of the double salt. The latter then begins gradual

TABLE 8

XRD patterns for the prepared double salt, $K_2Pb(SO_4)_2$ and Pb oxides

| No. | $K_2Pb(SO_4)_2$ | | $PbO_{1.55}$ | | $PbO_{1.44}$ | |
|---|---|---|---|---|---|---|
| | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ |
| 1 | 3.107 | 100 | 1.58 | 10 | 1.56 | 11 |
| 2 | 4.30 | 30 | 1.37 | 15 | 1.54 | 11 |
| 3 | 2.74 | 65 | 1.35 | 15 | 1.65 | 70 |
| 4 | 2.55 | 30 | | | | |
| 5 | 2.51 | 20 | | | | |
| 6 | 2.06 | 30 | | | | |
| 7 | 1.90 | 35 | | | | |
| 8 | 1.77 | 90 | | | | |
| 9 | 1.73 | 30 | | | | |
| 10 | 1.65 | 30 | | | | |

decomposition after 870°C; at 1050°C it loses about 3.0 wt.%; the decomposition product consists of α-$K_2SO_4$, $PbO_{1.55}$ and $PbO_{1.44}$.

## REFERENCES

1 C. Duval, Inorganic Thermogravimetric Analysis, 2nd edn., Elsevier, New York, 1963, p. 619.
2 Ref. 1, p. 620.
3 ASTM Card 22-498; ASTM Card 20-902.
4 R.M. Al-Shukry and F. Jasim, Thermochim. Acta, 37 (1980) 97.
5 F.G.H. Chr. Knaker Goard, Chem. Abstr., 48-4 (1954) 8612.
6 ASTM Card 5-577.
7 C. Duval, Inorganic Thermogravimetric Analysis, 2nd edn., Elsevier, New York, 1963.
8 G.V. Samsonov, The Oxides Handbook, IFI/Plenum, Oxford, 1973, pp. 110–115.
9 ASTM Card 27-1200.
10 ASTM Card 27-1201.
11 ASTM Card 23-331
12 G.B. Samsonov, The Oxides Handbook, IFI/Plenum, Oxford, 1973, p. 505.
13 ASTM Card 21-1165.
14 ASTM Card 7-599.
15 ASTM Card 1-717.
16 ASTM Card 12-1250.
17 ASTM Card 25-681.
18 ASTM Card 18-1217.