Thermochimica Acta, 86 (1985) 155–162
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TG, DTG AND DTA STUDIES OF PdO–$Na_2/K_2/S_2O_8$ BINARY REACTIONS

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(Received 4 October 1984)

ABSTRACT

TG, DTG and DTA investigations for PdO alone and binary PdO–$Na_2/K_2/S_2O_8$ mixtures of various molar ratios have been carried out derivatographically; the stoichiometric ratios have been found to be 1:1. PdO has catalytically lowered T_i values of decomposition of either $Na_2S_2O_8$ or $K_2S_2O_8$ by about 20°C. In the absence of moisture PdO reacts with $Na_2S_2O_8$ at about 80°C to form brittle masses whose formula can be tentatively written as $Na_4[PdO(SO_4)]_2$ which is stable up to 155°C. Such a complex has not been detected with the PdO–K_2/S_2O_8 system. At elevated temperatures, pyrosulfates of sodium and potassium react with PdO in the solid state yielding $PdSO_4$ (thermal stability 490–540°C) which subsequently decomposes into PdO and SO_3. The eutectics ($PdSO_4 + K_2S_2O_7$) and ($PdSO_4 + Na_2S_2O_7$) have been identified. In the presence of excess Pd, partial decomposition of melting of Na_2SO_4 occurs with the formation of Na_2PdO_2 and SO_2. X-ray diffractometry and IR spectrophotometry have been employed to identify intermediate and final products.

INTRODUCTION

According to the literature surveyed, PdO acts as an active oxidiser, catalyser, and, in the presence of hydrogen, a reducer for many reactions [1,2]. Because of its high electrical conductivity over a wide range of temperatures it is largely used in the production of thick-film glazed resistors and ceramics. Bayer and Wiedemann [3] studied the effect of O_2 on the thermal decomposition and oxidation of PdO. Jasim and co-workers [4–8] investigated the thermal behaviour of many metallic oxides in binary mixtures with $Na_2S_2O_8$ and $K_2S_2O_8$. Palladium sulfate is the least thermally studied palladium salt [9]. $PdSO_4 \cdot 2H_2O$ (brown-green crystals) is usually prepared [10] by dissolving Pd in ($H_2SO_4 + HNO_3$) mixtures. The crystals are dehydrated by concentrated H_2SO_4 at 250°C. To our knowledge, the

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0040-6031/85/$03.30

high-temperature reactions of PdO–$Na_2S_2O_8$ and $K_2S_2O_8$ systems have not yet been studied. It is the aim of this research to study these and sort out the stoichiometric reactions, to identify intermediate and final products and study their thermal stabilities and other properties.

EXPERIMENTAL

All chemicals were commercially available. Potassium and sodium persulfates were obtained from Hopkin and Williams, and PdO (puriss) from Fluka. Sample weight was 100 mg.

The apparatus and procedure employed were as described elsewhere [7]. IR spectra were obtained using a Perkin-Elmer (Model 1320 IR) spectrophotometer and the disc pellet technique.

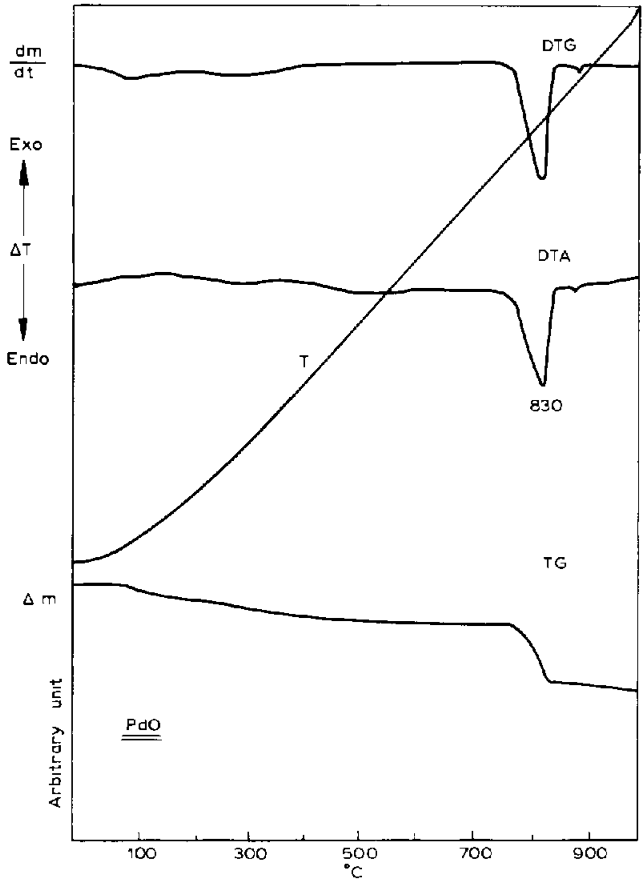

Fig. 1. Thermogram of PdO.

RESULTS AND DISCUSSION

The black PdO · xH_2O powder has a distorted PdO structure [11] formed due to solid solution with xH_2O. Figure 1 represents the TG, DTG and DTA curves of PdO · xH_2O which show slow decomposition attributable to loss of H_2O (8% = 3 mg) which is equivalent to 0.5 H_2O ($x = 0.5$) between 40 and 500°C. This indicates that H_2O is strongly bound to PdO. The horizontal plateau (500–780°C) shows the thermal stability of anhydrous PdO which starts decomposition at 780°C forming palladium metal [12–14] and O_2 with a total weight loss of 12 mg; this is accompanied by a large endotherm on the DTA curve (780–870°C) which indicates the affinity between Pd and O atoms.

PdO–$K_2S_2O_8$ system

Figure 2 depicts the TG and DTA curves of the various molar ratios investigated (Table 1). Table 1 indicates that PdO could catalytically lower

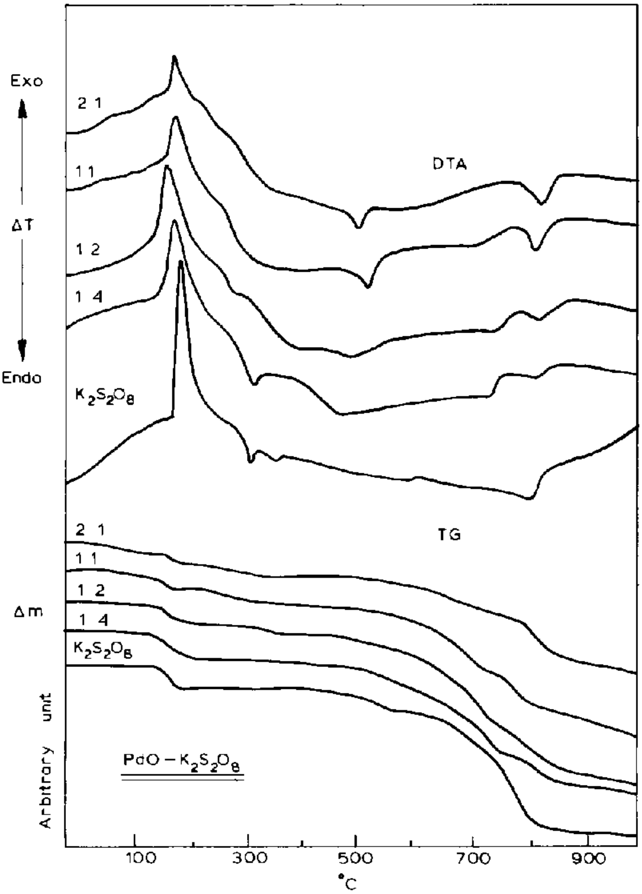

Fig. 2. TG and DTA curves of PdO–$K_2S_2O_8$ mixtures.

the T_i value of $K_2S_2O_8$ by about 10–20°C due to the great electrical conductance of the former at elevated temperatures [3]. The degree of lowering depends upon the oxide–persulfate ratio. The reactions between PdO and the $K_2S_2O_7$ produced for the ratios 1 : 4, 1 : 2, 1 : 1, and 2 : 1 occurred in the solid state (220°C) before the α–β crystalline phase change of $K_2S_2O_7$ and just within the melting of the latter ($T_{max} = 345°C$) where thermal neutralities take place. Calculations abstracted from TG curves indicate that about 32.727, 37.83, 41.09 and 54.93% $K_2S_2O_7$ had reacted with PdO for the ratios 1 : 4, 1 : 2, 1 : 1 and 2 : 1, respectively. Samples sintered at 450 and 770°C of the stoichiometric molar ratio (1 : 1) were found to be brownish coloured powders which gave XRD patterns (Table 2) and IR absorption bands (Table 3) belonging to $PdSO_4$. The stoichiometric reaction can be written as follows

$$PdO + K_2S_2O_7 \xrightarrow{\Delta} PdSO_4 + K_2SO_4$$

Further evidence for the formation of $PdSO_4$ (exclusion of others) could be obtained from quantitative computations of TG curves, XRD patterns, colours of the expected materials that might form entities such as potassium palladite, double salts, sulfides [9,10]. $PdSO_4$ prepared from the molar ratios

TABLE 1

Preparation and results of thermal analysis of binary $PdO–K_2S_2O_8$ systems

$PdO + K_2S_2O_8$ ratio	PdO (mg)	$K_2S_2O_8$ (mg)	Total wt. of mixture	O_2 lost (mg)		SO_3 lost (mg)		Decomp. temp. (°C)	
				Theor.	Exp.	Theor.	Exp.	T_i	T_f
0:1	0.0	100	100	5.92	5.7	29.59	29.0	160	180
1:4	10.17	89.83	100	5.32	4.8	26.58	18.0	140	210
1:2	18.46	81.54	100	4.83	4.0	24.13	15.0	145	190
1:1	31.17	68.83	100	4.07	3.6	20.37	12.0	150	200
2:1	47.52	52.48	100	3.11	3.1	15.53	7.0	145	200

TABLE 2

Bright *d*-lines for intermediate and final products obtained during thermal analysis

Compound	Bright *d*-lines (Å)
Pd	1.933, 2.231, 2.236
PdO	2.634, 2.718, 1.675
$PdO \cdot xH_2O$	2.619, 1.654, 1.552
$PdSO_4$	6.74, 5.15, 3.575
$Na_4[PdO(SO_4)]_2$	3.138, 5.964, 3.645, 3.827, 2.365
Na_2PdO_2	3.378, 4.741, 2.184
K_2SO_4	2.06, 2.855, 1.992

1 : 2, 1 : 1 and 2 : 1 decomposed just after melting at 500–780, 500–765 and 500–765°C, respectively, forming PdO and SO_3. The former was identified by XRD analysis (Table 2). At higher temperatures it decomposed forming Pd [12] and O_2. The *d*-lines belonging to α-K_2SO_4 were also identified [15] (Table 2). Eutectic ($PdSO_4 + K_2S_2O_7$) mixtures with melting endotherms at $T_{max} = 500$, 530 and 510°C for molar ratios 1 : 2, 1 : 1 and 2 : 1, respectively, were observed on the DTA curves. It could be noted from the curves that the endotherms become sharper as the PdO : $K_2S_2O_8$ ratios increased, which proves that more $PdSO_4$ is formed at higher ratios and the excess PdO catalysed the forward reaction ($PdO + K_2S_2O_7$). The kinetics of the thermal decomposition of $K_2S_2O_7$ take place in one large continuous step in the presence of PdO catalyst instead of its usual two steps.

PdO–$Na_2S_2O_8$ system

Figure 3 depicts the TG and DTA curves for the PdO–$Na_2S_2O_8$ mixtures (Table 4). This system exhibited a rather different behaviour from its predecessor because samples heated up to 105°C lose moisture and assume coherent hard masses which are thermally stable at lower molar ratios (plateau on TG curves). The small shoulders between 105 and 155°C indicate exothermic reactions and formation of a complex. XRD patterns for samples heated to 130°C showed the presence of PdO, $Na_2S_2O_8$ and an unknown complex formed through the reaction in the solid state

$$2\,PdO + 2\,Na_2S_2O_8 \underset{>155°C}{\overset{<155°C}{\rightleftharpoons}} Na_4[PdO(SO_4)]_2 \text{ (tentative formula)}$$

TABLE 3

IR absorption bands (cm^{-1}) of $PdSO_4$ obtained in this work and those found in the literature [20]

Literature values	1160	1105	1035	966
This work values	1155	1105	–	966

TABLE 4

Preparation and results of thermal analysis of binary PdO–$Na_2S_2O_8$ systems

PdO+ $Na_2S_2O_8$ ratio	PdO (mg)	$Na_2S_2O_8$ (mg)	Total wt. of mixture	O_2 lost (mg)		SO_3 lost (mg)		Decomp. temp. (°C)	
				Theor.	Exp.	Theor.	Exp.	T_i	T_f
0:1	0.0	100	100	6.92	6.5	33.6	31.0	160	260
1:4	11.39	88.61	100	5.95	4.0	29.77	4.8	160	220
1:2	20.45	79.55	100	5.35	3.7	26.73	5.3	150	220
1:1	33.45	66.05	100	4.44	3.5	22.19	4.0	140	220
2:1	50.69	49.31	100	3.31	2.5	16.57	2.0	135	220

The amount of O_2 liberated from the decomposition of $Na_2S_2O_8$ in the presence of PdO was found to be less than that liberated from $Na_2S_2O_8$ alone. The proposed complex starts decomposition at 160°C (with the decomposition of remaining $Na_2S_2O_8$)

$$Na_4[PdO(SO_4)]_2 \xrightarrow{155°C} PdSO_4 + Na_2PdO_2 + Na_2SO_4$$

XRD patterns for samples sintered at 130 and 155°C were different (Table 3), where the lines for $Na_2S_2O_8$ disappeared and those of $Na_2S_2O_7$ appeared as well as those belonging to $PdSO_4$, Na_2PdO_2 and Na_2SO_4 [3,16,18]. The *d*-lines for samples sintered at 130°C are: 3.005, 3.21, 3.398, 3.5, 3.6, 3.689, 3.827, 4.76, 2.116, 2.263, 2.365, 2.453, 2.616, 2.627, 2.72, 2.81, 1.916 and 2.013 Å.

As a complementary test for the formation of the tentative complex, samples for 1 : 1 ratio were analysed by IR spectrometry (Fig. 4). It can be

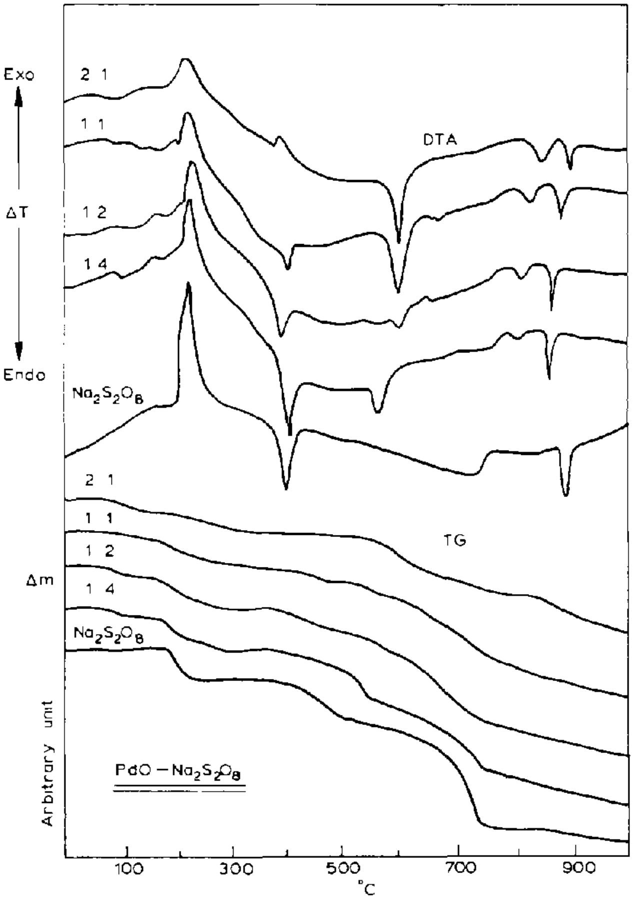

Fig. 3. TG and DTA curves of PdO–$Na_2S_2O_8$ mixtures.

shown from the IR spectra that the main absorption bands of the heated samples differ from those of the unheated ones which contain $Na_2S_2O_8$ and PdO mixture. However, PdO absorbs at longer wavelengths beyond 650 cm^{-1} and therefore does not interfere [19].

Samples of various molar ratios sintered between 330 and 500°C and analysed by XRD gave $PdSO_4$ *d*-lines (6.74, 5.15, 3.575, 3.34 and 2.897 Å) as well as Na_2SO_4 *d*-lines (1.88, 2.769, 3.045, 3.184 and 4.74 Å). The *d*-lines of $Na_2S_2O_7$ faded gradually. Since 1 : 1 is the stoichiometric molar ratio, the reaction for the formation of $PdSO_4$ is as follows

$$PdO + Na_2S_2O_7 \xrightarrow{\Delta} PdSO_4 + Na_2SO_4$$

At 390°C a large melting endotherm of $Na_2S_2O_7$ was observed indicating that the reaction occurred in the solid state. Next comes a weight loss due to partial decomposition of $Na_2S_2O_7$. The horizontal plateau extending between 490 and 540°C represents the thermal stability of $PdSO_4$. The endothermic peak at $T_{max} = 590$°C is attributable to the simultaneous melting and decomposition of $PdSO_4(PdO + SO_3)$ within a eutectic of $PdSO_4 + Na_2S_2O_7$. This relatively large endotherm supported the 1 : 1 stoichiometry of the

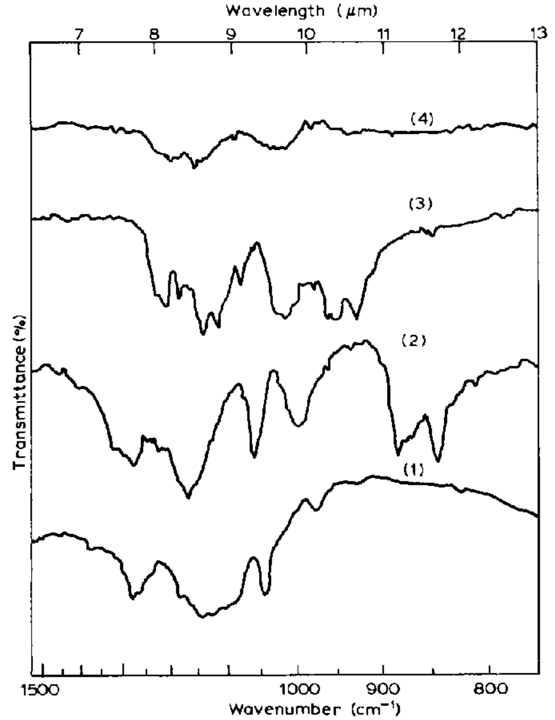

Fig. 4. IR spectra of the PdO–$Na_2S_2O_8$ system at various ratios and temperatures. (1) Pure $Na_2S_2O_8$, (2) 1 : 4 molar ratio at 130°C, (3) 2 : 1 molar ratio at 450°C, (4) 1 : 4 molar ratio at 500°C.

above reaction, since it is the largest of the ratios studied. Thereafter, the unreacted $Na_2S_2O_7$ was entirely decomposed at 780°C. Samples sintered above 770°C and analysed by XRD confirmed the presence of PdO alone. The endothermic peak at 800–840°C indicates the degradation of PdO into Pd and O_2, whereas that at $T_{max} = 880°C$ belongs to the melting of Na_2SO_4 which shows the absence of a eutectic at this temperature. In the presence of a large excess of PdO (2 : 1 ratio) the liberated PdO reacts with the melting Na_2SO_4 (880°C) causing partial decomposition of the latter [16]

$$Pd + Na_2SO_4 \xrightarrow{880°C} Na_2PdO_2 + SO_2$$

$$SO_2 + 1/2\ O_2 \rightarrow SO_3 + \text{heat}$$

The exotherm of the latter does not show because of thermal neutrality.

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