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THERMAL AND X-RAY STUDIES OF REACTIONS BETWEEN TERBIUM(III,IV) OXIDE AND PERSULFATES OF SODIUM AND POTASSIUM

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ABSTRACT

The solid state high temperature reactions between Tb_4O_7 and $Na_2S_2O_8$ or $K_2S_2O_8$ have been investigated using TG, DTG, DTA and XRD techniques over the temperature range ambient to 1020°C. Different $Tb_4O_7 : Na_2/(K_2)/S_2O_8$ molar ratios have been analyzed. The 1 : 6 ratio is found to be the one that gives stoichiometric reactions with either of these persulfates with the formation of $Na_2Tb_2(SO_4)_4$ or $KTb\,(SO_4)_2$. Both double salts are thermally stable to the ceiling temperature of the heating programme. Intermediate and final products are identified by X-ray diffractometry.

INTRODUCTION

Terbium(III,IV) oxide (Tb_4O_7) is a dark brown color and changes to terbium(III) oxide (Tb_2O_3) at about 600°C in H_2 gas atmosphere [1]. Tb_4O_7 is almost thermally stable to about 1000°C, nevertheless a slight decomposition of the oxide ($\sim 2\%$) is observed over the temperature range 505–890°C, due to the formation of Tb_2O_3 and $TbO_{1.823}$, respectively. The catalytic effect of Co_3O_4, Sc_2O_3, CuO, ZnO, TiO_2, Dy_2O_3 and other Ln_2O_3 oxides on the thermal decomposition of persulfates to pyrosulfates, and the possibility of the latter to react with these oxides have been studied previously [2–5].

The aim of the present work is to investigate the role of the dual valency character of the terbium ion in Tb_4O_7 when reacting with the alkali persulfates at high temperatures, and therefore the types of compounds that may be formed under these conditions.

EXPERIMENTAL

Materials

$Na_2S_2O_8$ and $K_2S_2O_8$ were Hopkin and Williams AnalaR. Tb_4O_7 (purity = 99.9%) was supplied by Koch-Light. α-Al_2O_3 (BDH), sintered at 1200°C, was used as reference material.

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Apparatus and methods

The experiments were performed on a photographic recording MOM derivatograph in a static atmosphere of air. The temperature was programmed linearly at 10°C min^{-1} from ambient to 1020°C. MOM type 3 platinum crucibles were used for sample and reference. The weight of the sample mixture was 200 mg. Mixtures of Tb_4O_7 and sodium or potassium persulfate with mole ratios of 1 : 12, 1 : 6, 1 : 3, 2 : 3 and 1 : 1 were systematically prepared by careful grinding of the calculated amounts of the oxide and persulfate for 20 min in an agate mortar to 200–300 mesh followed by drying at 80°C for 4 h. Sensitivities used were: TG 200 mg, DTA 1/10 and DTG 1/10. X-Ray diffractograms were obtained using a Philips diffractometer with nickel-filtered CuK_α radiation. The setting of the instrument was 40 kV and 20 mA with a scanning speed of 2θ min^{-1}.

RESULTS AND DISCUSSION

Figures 1 and 2 show the TG and DTA curves for sodium and potassium persulfates in intimate admixtures with Tb_4O_7 in oxide persulfate molar ratios of 1 : 12, 1 : 6, 1 : 3, 2 : 3 and 1 : 1, respectively. Details of the thermal decomposition products are given in Tables 1 and 2.

From the exotherms of the DTA curves of molar ratios 1 : 12, 1 : 6 and 1 : 3, it appears that the reaction between the oxide and thermally produced pyrosulfate occurs after the fusion temperature of the latter. As for the molar ratios 2 : 3 and 1 : 1, the reaction occurs within the fusion temperature of the pyrosulfate, resulting in the disappearance of its fusion endotherm due to thermal neutrality.

TABLE 1

Preparation of molar ratios of the system Tb_4O_7–$Na_2S_2O_8$ and thermal decomposition products obtained on subjecting the system to the heating programme

Mole ratio Tb_4O_7 : $Na_2S_2O_8$	O_2 lost (mg)		SO_3 lost (mg)		Decompn. temp. of $Na_2S_2O_8$ (°C)		Reaction temp. of Tb_4O_7–$Na_2S_2O_7$ (°C)	
	Pract.	Theor.	Pract.	Theor.	T_i	T_f	T_i	T_f
0 : 1	13.0	13.4	67.0	67.2	190	225		
1 : 12	11.0	10.7	29.0	53.3	190	240	385	450
1 : 6	9.0	8.8	9.0	44.1	180	230	390	450
1 : 3	6.0	6.6	8.0	32.8	195	240	390	430
2 : 3	4.0	4.3	5.0	21.6	200	235	362	400
1 : 1	4.0	3.2	5.0	16.2	220	270	360	395

TABLE 2

Preparation of molar ratios of the system Tb_4O_7–$K_2S_2O_8$ and the thermal decomposition products obtained on subjecting the system to the heating programme

Mole ratio Tb_4O_7: $K_2S_2O_8$	O_2 lost (mg)		SO_3 lost (mg)		Decompn. temp. of $K_2S_2O_8$ (°C)		Reaction temp. of Tb_4O_7: $K_2S_2O_8$ (°C)	
	Pract.	Theor.	Pract.	Theor.	T_i	T_f	T_i	T_f
0 : 1	12.0	11.8	59.0	59.1	180	200		
1 : 12	10.0	9.7	26.0	48.6	170	210	345	420
1 : 6	8.0	8.1	6.0	40.3	170	215	340	410
1 : 3	6.5	6.2	5.0	31.0	180	235	340	360
2 : 3	4.5	4.2	5.7	20.9	170	230	290	320
1 : 1	3.0	3.1	6.0	15.7	190	240	[a]	[a]

[a] Due to thermal neutrality.

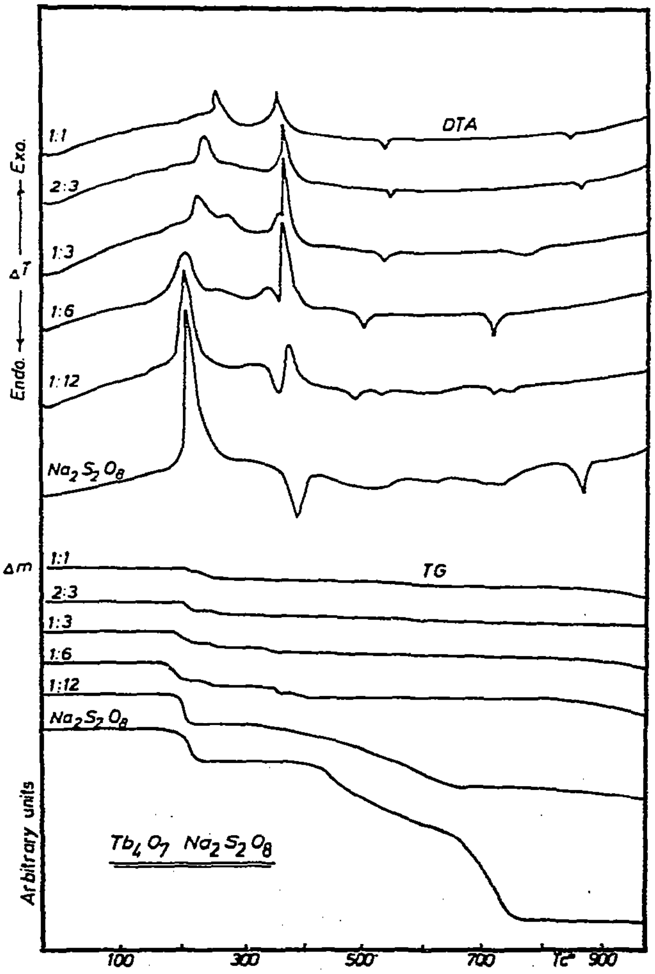

Fig. 1. TG and DTA curves of terbium(III, IV) oxide–sodium persulfate mixtures.

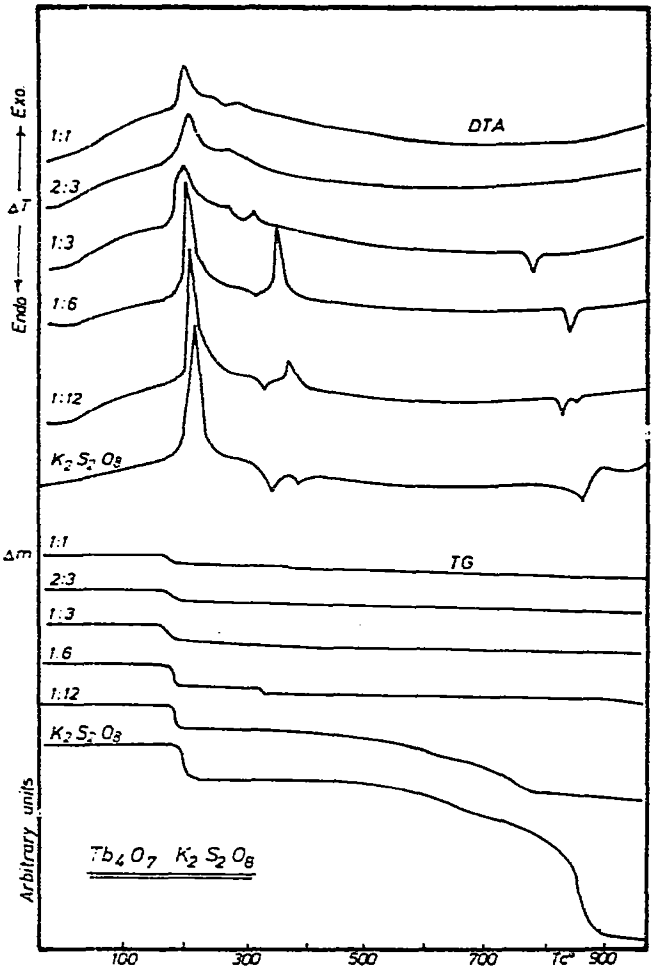

Fig. 2. TG and DTA curves of terbium(III, IV) oxide–potassium persulfate mixtures.

Tb_4O_7–$Na_2S_2O_8$ system

Experiments with 1:6 Tb_4O_7:$Na_2S_2O_8$ showed that 80% of the pyrosulfate of sodium reacted with the oxide (stoichiometric molar ratio) to yield the compound $Na_2Tb_2(SO_4)_4$ according to the reaction

$$Tb_4O_7 + 6\,Na_2S_2O_7 \xrightarrow{\Delta} 2\,Na_2Tb_2(SO_4)_4 + 4\,Na_2SO_4 + 0.5\,O_2$$

The identity of this double salt was confirmed by XRD patterns, as seen in Table 3, for specimens sintered between 390 and 450°C, i.e. in the vicinity of the largest exotherm on the DTA curve [6].

As for the 1 : 12 ratio, 45% of the pyrosulfate produced reacts with the oxide. This is indicated by the relatively small exotherm between 385 and 450°C. Afterwards, a small endotherm shows up at 515°C which most probably indicates a crystalline phase transition of the double salt mentioned above.

TABLE 3

Data for XRD patterns obtained for the 1:6 Tb_4O_7:$Na_2S_2O_8$ ratio sintered at 560°C

d(Å)	3.503	3.045	2.803	2.777	2.184
I/I_0	80	84	100	75	66

The first exo-peak of the DTA curve in the 1:6 mole ratio, which appears between 180 and 230°C, indicates the persulfate decomposition to pyrosulfate and atomic oxygen, and the subsequent combination of the latter by an exothermic process to form molecular oxygen. However, as appears from TG and DTA, this decomposition takes place in two steps, a large decomposition step referring to the small catalytic effect of the oxide to retard the decomposition at lower temperatures, and a small step due to retarding catalysis, presumably due to an intermediate unstable persulfate–oxide complex. The retardation effect increases with increase of the oxide content; this is seen from both TG and DTA curves of the other molar ratios.

The endotherm of DTA which appears at 520°C refers to a crystalline phase transition. This phase transition, affirmed by XRD patterns, was obtained for samples sintered before and after the endotherm. The endotherm appearing at 750°C corresponds to the melting point temperature of impure (or perhaps eutectic of) Na_2SO_4 and $Na_2Tb_2(SO_4)_4$. The double salt was found to be stable till the end of the heating programme.

For the remaining mole ratios (1:3, 2:3, 1:1), the amounts of the double salt formed are relatively small, as judged from the TG curves and the heights of the exo-peaks of the double salt formation.

Tb_4O_7–$K_2S_2O_8$ system

The TG and DTA curves illustrated in Fig. 2 show several interesting features, the most striking of which is the 1:6 Tb_4O_7:$K_2S_2O_8$ molar ratio, where the stoichiometric reaction

$$Tb_4O_7 + 6\ K_2S_2O_7 \xrightarrow{\Delta} 4\ KTb\ (SO_4)_2 + 4\ K_2SO_4 + 0.5\ O_2$$

occurs between 340 and 410°C. The reaction is exhibited on the DTA curve as a large exo-peak appearing at 340°C after the crystalline β- to α-$K_2S_2O_7$ phase change. Thereafter a horizontal plateau is seen on the DTA curves up to 870°C, then a sharp endotherm appears which indicates the crystalline phase change of the double salt. Samples sintered at 500°C, i.e. within this thermal stability range, when analyzed by XRD indicate the presence of a double salt, KTb $(SO_4)_2$, as a major constituent of the sample. The evolution of O_2 gas is registered on the TG curve of 1:6 ratio as a loss in weight which is equal to 8.0 mg. The crystalline phase change endotherms of the double salt in molar ratios 2:3 and 1:1 may be attributed to the fact that such small amounts of the salt are formed that they could not be detected by the DTA sensors.

Comparing the positions of the exotherms of the various ratios (Figs. 1 and 2), it is clear that as the amount of oxide increases, the maximum temperature of the reaction is lowered; this could probably be attributed to the catalytic effect of Tb_4O_7.

It is concluded that, as expected, the oxide exhibits the catalytic activity of a *p*-type semiconductor which is similar to that of CeO_2.

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