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THERMAL AND X-RAY STUDIES OF REACTIONS BETWEEN SCANDIUM(III) OXIDE AND SODIUM OR POTASSIUM PERSULFATES

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ABSTRACT

TG, DTG, and DTA experiments were carried out to elucidate the influence of Sc_2O_3 on the thermal decomposition of $Na_2S_2O_8$ and $K_2S_2O_8$ under a static (air) atmosphere from ambient to 1050°C, using a derivatograph. X-Ray diffractometry has been employed to identify the intermediate and final decomposition products. Different Sc_2O_3 : $Na_2(K_2)S_2O_8$ molar ratios were investigated and the 1 : 3 ratio found to be the one that gives stoichiometric reactions with either of these salts. Sc_2O_3 was found to react at 250 and 440°C with the thermally produced $Na_2S_2O_7$ yielding $Sc_2(SO_4)_3$. The scandium(III) sulfate was thermally stable up to 840°C. Similarly, the oxide reacts stoichiometrically at 420°C to produce $KSc(SO_4)_2$, a double salt which began to decompose at 840°. Moreover, three new crystalline phase-transformations were detected for $Sc_2(SO_4)_3$ at 640, 695, and 735°C.

INTRODUCTION

The effects of some oxides on the thermal decomposition of sodium and potassium peroxodisulfates (persulfates) and the behaviour of these oxides towards the thermally produced pyrosulfates have been investigated [1—3]. In addition, it has been found elsewhere [4] that Sc_2O_3 behaves like a *p*-type semi-conductor under 627°C; above that temperature the oxide acts as an insulator. A pronounced catalytic effect for this oxide has been revealed by the fact that it lowers the decomposition temperature of lithium carbonate from 1270 to 500°C [5]. Steinberg and Shidlovsky (see ref. 6) have studied the thermal decomposition of scandium perchlorate using TG and DTA and have found that the decomposition occurred after the melting point of the salt, but they did not discuss the behaviour of the individual oxide itself. This paper presents results of the thermal reactions of Sc_2O_3 with the persulfates of sodium and potassium, and the thermal stabilities of the intermediate and final products and it accounts for the distinct behaviour towards both salts.

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TABLE 1

Preparation of various Sc_2O_3 : $Na_2S_2O_8$ molar ratios and the amounts of O_2 and SO_3 evolved

Sc_2O_3 : $Na_2S_2O_8$	Sample wt. (mg)	$Na_2S_2O_8$ (mg)	O_2 evolved (mg)		SO_3 evolved (mg)		Decomp. temp. (°C)	
			Calc.	Found	Calc.	Found	T_i	T_f
1 : 6	200.0	180.400	12.25	13.00	61.28	40.50	200	240
1 : 3	199.5	167.21	11.23	11.50	56.18	18.00	200	295
2 : 3	200.0	144.29	9.95	10.00	48.47	10.00	200	245
1 : 1	200.0	122.17	8.21	9.20	41.04	7.80	215	290
2 : 1	200.0	92.67	6.22	6.50	31.13	2.00	240	265
3 : 1	200.0	72.73	4.88	4.00	24.40		255	285

TABLE 2

Preparation of various Sc_2O_3 : $K_2S_2O_8$ molar ratios and the amounts of O_2 and SO_3 evolved

Sc_2O_3 : $K_2S_2O_8$	Sample wt. (mg)	$K_2S_2O_8$ (mg)	O_2 evolved (mg)		SO_3 evolved (mg)		Decomp. temp. (°C)	
			Calc.	Found	Calc.	Found	T_i	T_f
1 : 6	201.0	163.33	9.66	9.50	48.33		190	220
1 : 3	199.5	170.54	10.09	10.00	50.46	3.00	180	220
2 : 3	199.5	148.87	8.81	8.50	44.05	2.00	180	220
1 : 1	200.0	132.45	7.84	7.50	39.19	2.00	190	230
2 : 1	200.0	98.99	5.86	6.00	29.29		190	230
3 : 1	200.0	79.04	4.68	5.00	23.39		190	225

EXPERIMENTAL

Materials

All chemicals were of AnalaR quality. α-Al_2O_3 was calcined at 1370°C; $Na_2S_2O_8$ and $K_2S_2O_8$ were supplied by BDH and Sc_2O_3 (99.9%) by Koch—Light.

Apparatus and methods

The experiments were performed on a MOM derivatograph in a static atmosphere of air with α-Al_2O_3 as the inert substance. The temperature was programmed linearily at $10^\circ\ \mathrm{min}^{-1}$ from ambient to 1050°C. The samples and reference materials were placed in standard platinum crucibles. The weight of the sample was 200 mg. Tables 1 and 2 give details of the preparation of the various oxide : persulfate systems. In each preparation, the mixture was ground carefully in an agate mortar to pass a 200 mesh sieve, and was then dried at 80°C for 3 h. Sensitivities of the methods were: TG 200 mg, DTA 1/10, and DTG 1/10.

The X-ray analysis of the sinters was carried out on a Philips X-ray diffractometer using 40 kV CuK_α radiation filtered through a nickel filter; signal recording was done with a scintilation counter at a chart paper speed of 20 mm min^{-1}. The XRD patterns were recorded for the 2θ angles from 2 to 52°. The XRD patterns of the sinters were compared with the corresponding ASTM cards. Slides were prepared by dispersing the powdered samples in acetone which was then spread on a small circular glass sheet in an even layer 2 mm thick and left to dry. After X-ray exposure, the sheet should be discarded to prevent cross-contamination and hence lower the background noise.

RESULTS AND DISCUSSION

The Sc_2O_3—$Na_2S_2O_8$ system

The non-isothermal behaviour of the various Sc_2O_3 : $Na_2S_2O_8$ molar ratios are illustrated in Fig. 1. The DTA curves show several endothermic and exothermic peaks. From the exotherms of the DTA curves of molar ratios 1 : 6, 2 : 3, and 1 : 1, it appears that the reaction between the oxide and the thermally produced pyrosulfate occurs after the fusion temperature of the latter. On the other hand, in the molar ratios 2 : 1 and 3 : 1, it occurs within the fusion temperature of the pyrosulfate, resulting in the disappearance of its fusion endotherm due to thermal neutrality.

As is evidenced by the XRD patterns (Table 3) and TG curves, calculations indicate that the 1 : 3 Sc_2O_3 : $Na_2S_2O_8$ molar ratio is the stoichiometric one that leads to the irreversible reaction

$$Sc_2O_3(s) + 3\ Na_2S_2O_7(s, l) \rightarrow Sc_2(SO_4)_3(s) + 3\ Na_2(SO_4)(s)$$

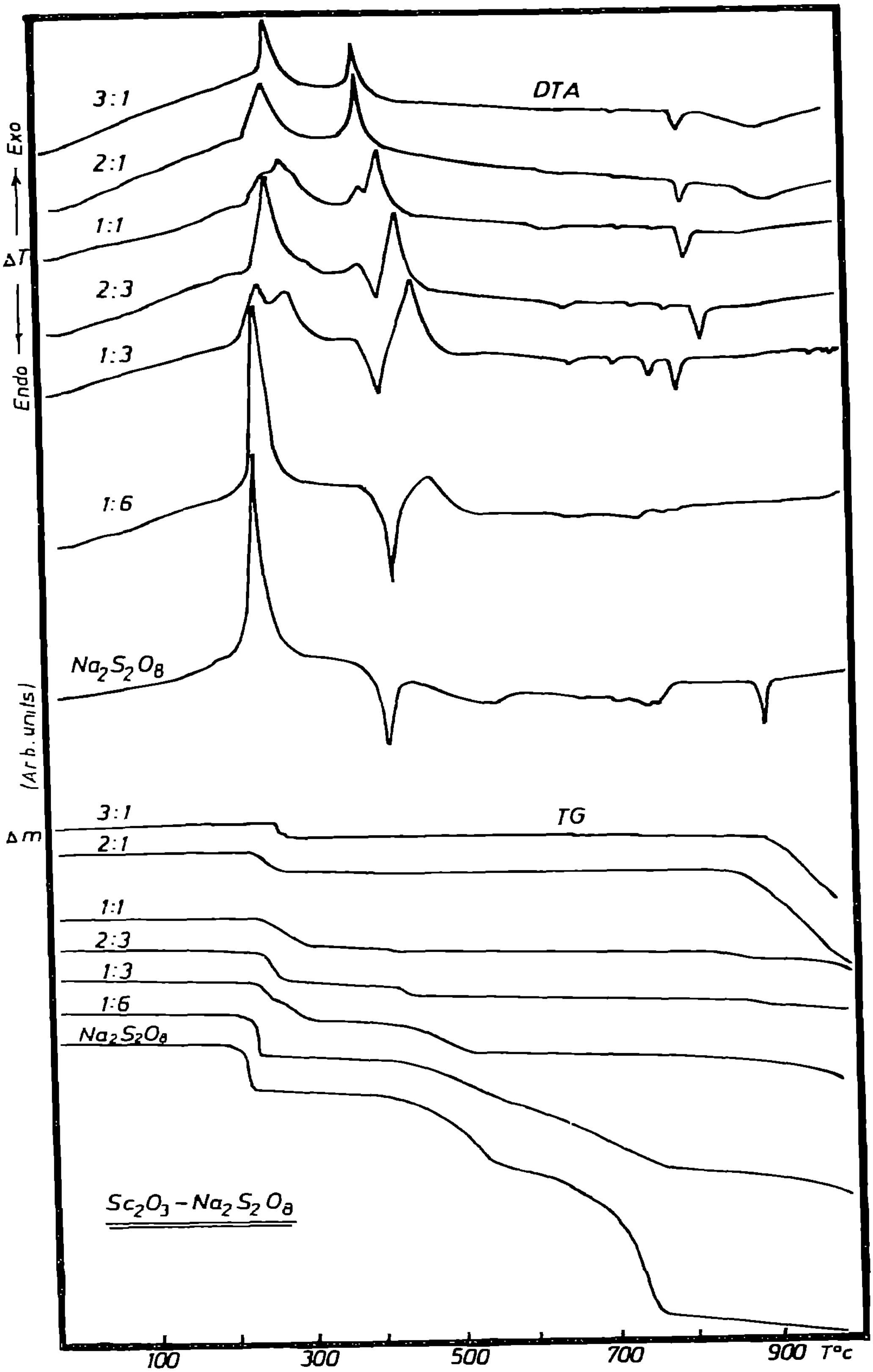

Fig. 1. TG and DTA curves of scandium(III) oxide—sodium persulfate mixtures.

TABLE 3

Data for XRD patterns obtained for the 1 : 3 Sc_2O_3 : $Na_2S_2O_8$ system sintered at 800°C

d (A)	4.7460	3.7887	3.1184	2.9683	2.8030	2.2243
I/I_0	43	100	77	70	45	28

that occurs at 250 and 440°C, respectively.

For the 1 : 6 ratio, only a small fraction of the pyrosulfate produced reacts with the oxide as indicated by the exotherm at 445°C. Afterwards, small ripples of endotherms show up due to the formation of small amounts of $Sc_2(SO_4)_3$. However, in the 1 : 3 molar ratio, these endotherms become larger and more distinct due to the relatively large quantities of scandium sulfate.

Samples sintered at 250°C give XRD data that confirm the formation of $Sc_2(SO_4)_3$ as well as the presence of unreacted sodium pyrosulfate and sodium persulfate. This is actually inferred in the 1 : 3 ratio by the appearance of twin exothermic peaks instead of the usual large exotherm (attributed to oxygen formation through a secondary reaction) of the persulfate decomposition at 250°C. The first small exotherm is undoubtedly contributed by persulfate decomposition, whereas the second is a result of scandium(III) sulfate formation. Thereafter, the remaining oxide reacts with the pyrosulfate, a fact which is represented by a sharp exotherm at 440°C and confirmed by XRD patterns for samples sintered at this temperature. The two reactions at 250 and 440°C are clearly represented by the TG curve of the 1 : 3 ratio sample. From 550°C onwards, a horizontal plateau indicates the thermal stability of the $Sc_2(SO_4)_3$ which begins to decompose at 840°C. The salt undergoes three crystalline phase transformations successively at 640, 695, and 735°C, a fact which is indicated by three small endotherms. Since the last endotherm represents the largest enthalpy change, it is thermally the most stable phase of the three. However, the endotherms degenerate as we go towards higher oxide contents. The identities of the three crystalline phases are affirmed by XRD patterns obtained for samples sintered at the respective temperatures. Further, the endotherm that appears at 770°C corresponds to the melting point of impure sodium sulfate resulting from the decomposition of unreacted sodium pyrosulfate. As far as we are aware, no mention has previously been made to the formation of three such crystalline phase-transformations of $Sc_2(SO_4)_3$. Moreover, it must be emphasised that no compound such as $Sc_2O(SO_4)_2$ has been identified, as declared elsewhere [7], throughout the complete heating programs of the Sc_2O_3 : $Na_2S_2O_8$ system. Decomposition of the $Sc_2(SO_4)_3$ begins at 840°C as

TABLE 4

XRD data for the thermal decomposition products of $Sc_2(SO_4)_3$ sintered at 1000°C

d (A)	2.8394	1.7384	4.0044	2.0970
I/I_0	100	42	17	15

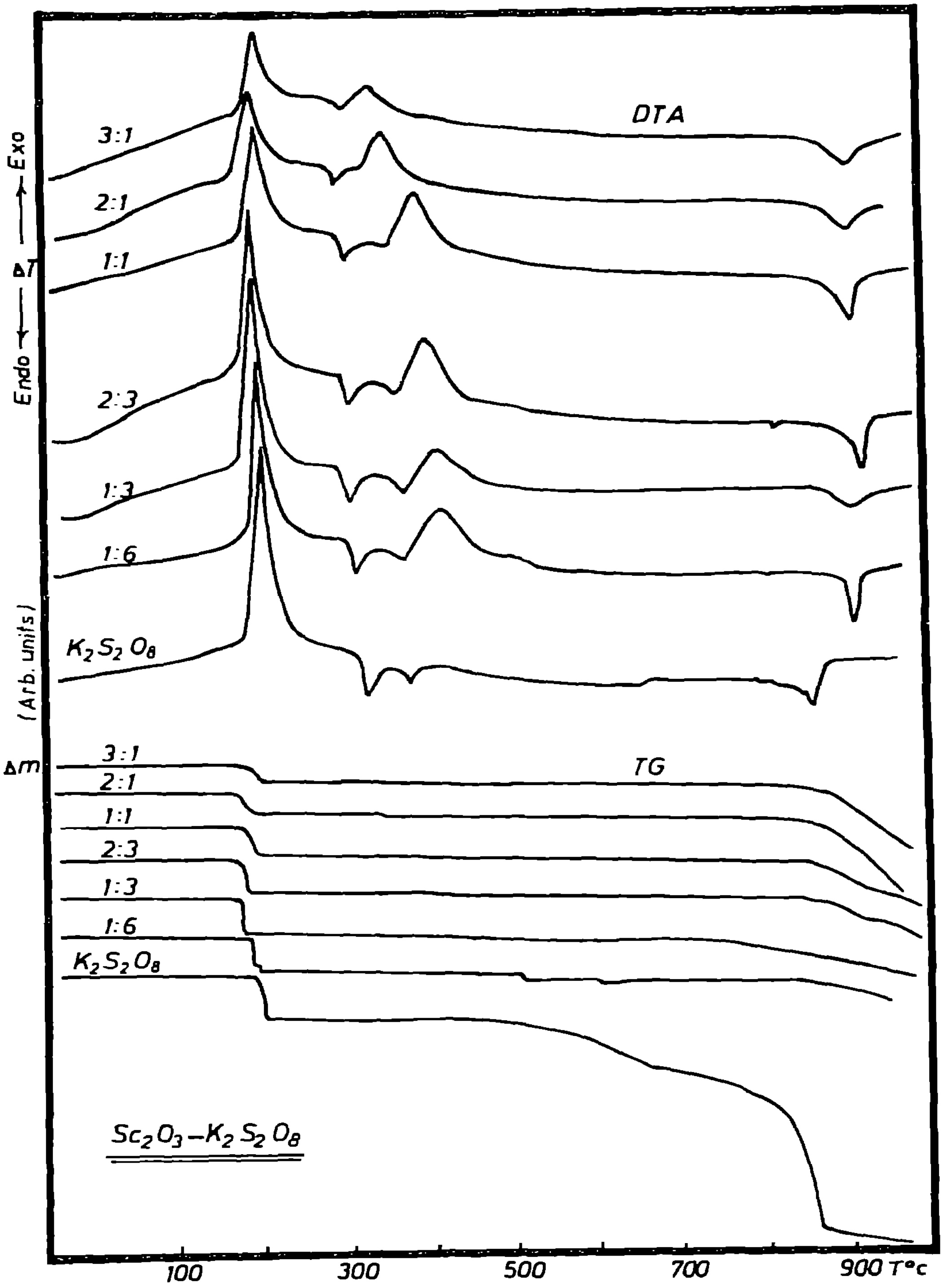

Fig. 2. TG and DTA curves of scandium(III) oxide—potassium persulfate mixtures.

shown by the weight loss during TG and the corresponding endotherm on the DTA at that temperature. The XRD data indicate that the decomposition is complete at 1000° (Table 4) where no sharp *d*-lines for the $Sc_2(SO_4)_3$ have been detected, but instead those of Sc_2O_3 appear, i.e.

$$Sc_2(SO_4)_3 \rightarrow Sc_2O_3 + 3\ SO_3$$

As shown by the molar ratios of 2 : 1 and 3 : 1, the decomposition is catalytically promoted by increasing the proportion of oxide in the mixture.

Since no initial or intermediate products other than $Sc_2(SO_4)_3$, Sc_2O_3, and $Na_2S_2O_7$ are identified under the prevailing non-isothermal conditions at 250°C, it is clear that the solid-state reaction of $Na_2S_2O_7$ with Sc_2O_3 is autocatalysed by the oxide at a heating rate of 10° min^{-1} by reducing the activation energy of both reactants, perhaps through unstable complex formation of intermediates, although X-ray analysis of sinters at 250°C could not reveal such an intermediate. It seems that the reaction between the oxide and pyrosulfate does not go to completion unless a temperature of 440°C is reached. This explains why the formation of scandium(III) sulfate takes place in two stages.

The Sc_2O_3—$K_2S_2O_8$ system

The TG and DTA curves illustrated in Fig. 2 show several interesting features of which the most striking is the 1 : 3 Sc_2O_3 : $K_2S_2O_8$ molar ratio where the stoichiometric reaction

$$Sc_2O_3(s) + 3\ K_2S_2O_7(l) \rightarrow 2\ KSc(SO_4)_2(s) + 2\ K_2SO_4(s)$$

occurs at 420°C, i.e. above the melting point of pure $K_2S_2O_7$. The reaction is observed as a broad exotherm on the DTA curve. Afterwards, a horizontal plateau is seen on the TG and DTA curves up to 840°C. Samples sintered at 515°C, i.e. within this thermal stability range, when analysed diffractometrically indicate the presence of a double salt, $KSc(SO_4)_2$, as a major constituent of the sample. Above 840°C, an attenuated shoulder of the TG curve and a corresponding flattened endotherm on the DTA curve refer to the gradual decomposition of this double salt. However, samples preheated up to the end of the program, still give XRD data that are identical with those of $KSc(SO_4)_2$; this eventually means that only negligible amounts of it really decompose.

On the other hand, the ratios investigated, other than that of 1 : 3, have shown almost similar behaviour.

Comparing the positions of the exotherms of the various ratios (Figs. 1 and 2), it is clear that as the amount of the oxide increases, the temperatures of reaction are reduced and this reduction could be attributed to a *p*-type catalytic effect of Sc_2O_3. Under similar non-isothermal conditions, it is observed, however, that $KSc(SO_4)_2$ has been formed whereas the corresponding sodium double salt has not. This dissimilarity may be ascribed to the fact that potassium has a greater ionic radius than sodium and that the scandium and potassium radii are almost equal, hence both K and Sc ions can fit snugly into the unit cell packing holes present between the sulfate ions of

$KSc(SO_4)_2$. This situation has no counterpart for the ionic radii of sodium and scandium. Further, the reaction between SC_2O_3 and $Na_2S_2O_7$ occurs at two widely differing temperatures, i.e. at 250 and 440° C, and that between the oxide and $K_2S_2O_7$ at 410° C, i.e. the melting point of the latter. This can be accounted for, at least hypothetically, by referring first to the basic electropositive character of Sc^{3+} in Sc_2O_3, and secondly, to the resemblance of ionic radii of scandium and potassium. Both factors hinder the diffusion of Sc^{3+} into the rigid solid phase of potassium pyrosulfate. This barrier continues until thermal deformation of the lattice structure of the pyrosulfate begins at 410° C, i.e. on melting.

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