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THERMAL AND X-RAY INVESTIGATION OF BINARY COBALTO-COBALTIC OXIDE—ALKALI PERSULFATE SYSTEMS

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ABSTRACT

It has been found that cobalt(II, III) oxide, Co_3O_4, lowers the thermal decomposition temperature of $Na_2S_2O_8$ and $K_2S_2O_8$ by about 25°C by catalysis, and it therefore acts as a P-type semiconductor at high temperature and atmospheric (air) pressure. Also, this oxide reacts at high temperature with sodium or potassium pyrosulfates to form thermally stable sodium cobalt disulfate, $Na_2Co(SO_4)_2$ and potassium cobalt trisulfate, $K_2Co_2(SO_4)_3$, respectively. Binary systems, consisting of a 1 : 3 mole ratio (oxide : persulfate), are established as representing the solid state stoichiometric reaction. X-Ray diffractometry is employed to identify intermediate and final reaction products in general. All calculations are based on data obtained from TG, DTG and DTA curves.

INTRODUCTION

In recent publications [1—3], the effects of many metal oxides on the thermal decomposition of alkali persulfates were studied derivatographically from ambient to 1000°C, which is the ceiling temperature of the heating program. The catalytic effect of NiO, TiO_2, CuO and ZnO on the thermal decomposition of persulfates to pyrosulfates and the possibility of the latter reacting with these oxides has also been studied. The semiconductive behaviour of these oxides at high temperatures, which is due to defects in the lattice structure, controls their catalytic activity [4] and therefore, affects the manner in which the mechanism of thermal decomposition of oxo-salts occurs.

Cobalt(II, III) has a normal spinel structure [5], as the most stable phase at high temperatures, and this changes [6] to cobalt(II) oxide, CoO, at 945°C. The equation

$$Co_3O_4 \underset{900^\circ C}{\overset{905\text{—}925^\circ C}{\rightleftharpoons}} 3\,CoO + \tfrac{1}{2}O_2$$

illustrates this conversion process [6]. Both oxides are P-type semiconductors. In this work, the effect of cobalt(II, III) oxide on the thermal decomposition of sodium and potassium persulfates is considered.

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EXPERIMENTAL

Reagents

The $Na_2S_2O_8$ and $K_2S_2O_8$ used were Analar grade supplied by Hopkin and Williams and the Co_3O_4 was analytical reagent grade supplied by BDH. α-Al_2O_3 (BDH) was used as a reference material. Cylindrical platinum crucibles were used as specimen holders.

Apparatus and method

TG and DTA curves were recorded by means of a Paulik—Paulik—Erdey (MOM) derivatograph under a static (air) atmosphere.

Mixtures of Co_3O_4 and sodium or potassium persulfate with mole ratios of 1 : 6, 1 : 3, 2 : 3, 1 : 1 and 2 : 1 were systematically prepared by careful grinding of the calculated amounts of oxide and persulfate for 20 min in an agate mortar to 200—300 mesh followed by drying at 80°C for 2 h.

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 2 θ min^{-1}.

RESULTS AND DISCUSSION

Working with sample weights of 200 mg at a heating rate of 10°C min^{-1}, the thermo-analytical curves obtained simultaneously are represented in Figs. 1 and 2 for the sodium and potassium persulfates systems, respectively.

The following data and conclusion are obtained from an evaluation of these curves obtained for simultaneous binary reaction systems. The oxide acts as a catalyst for the thermal transformation of persulfate to pyrosulfate and the initial decomposition temperature, T_i, as determined from the TG and DTG curves, is lowered by about 25°C compared with the pure persulfates. This is attributed to the catalytic activity of the oxide [4]. The intervals between the initial and final decomposition temperatures were measured for all mole ratios except 1 : 6 where the amount of oxide was relatively small and therefore its effect was negligible. However, the amount of oxygen liberated in the sodium persulfate decomposition was found to be slightly more than the theoretical value. This difference is most probably caused by partial decomposition of the Co_3O_4 at these temperatures as is indicated by the TG curve for the decomposition of pure Co_3O_4. A sharp endotherm at the melting point of $Na_2S_2O_7$ was always observed on the DTA curves and this was not affected by the presence of oxide. On the other hand, a polymorphic transition, β- to α-$K_2S_2O_7$, occurred at 320°C and the melting point of $K_2S_2O_7$ did not appear clearly on the corresponding DTA curves because the reaction between the oxide and $K_2S_2O_7$ reached a maximum rate before the melting point of the latter was reached. The reaction of sodium pyrosulfate with the oxide is shown as exotherms on the respective DTA curves (Fig. 1) at the temperature range shown in Table 1.

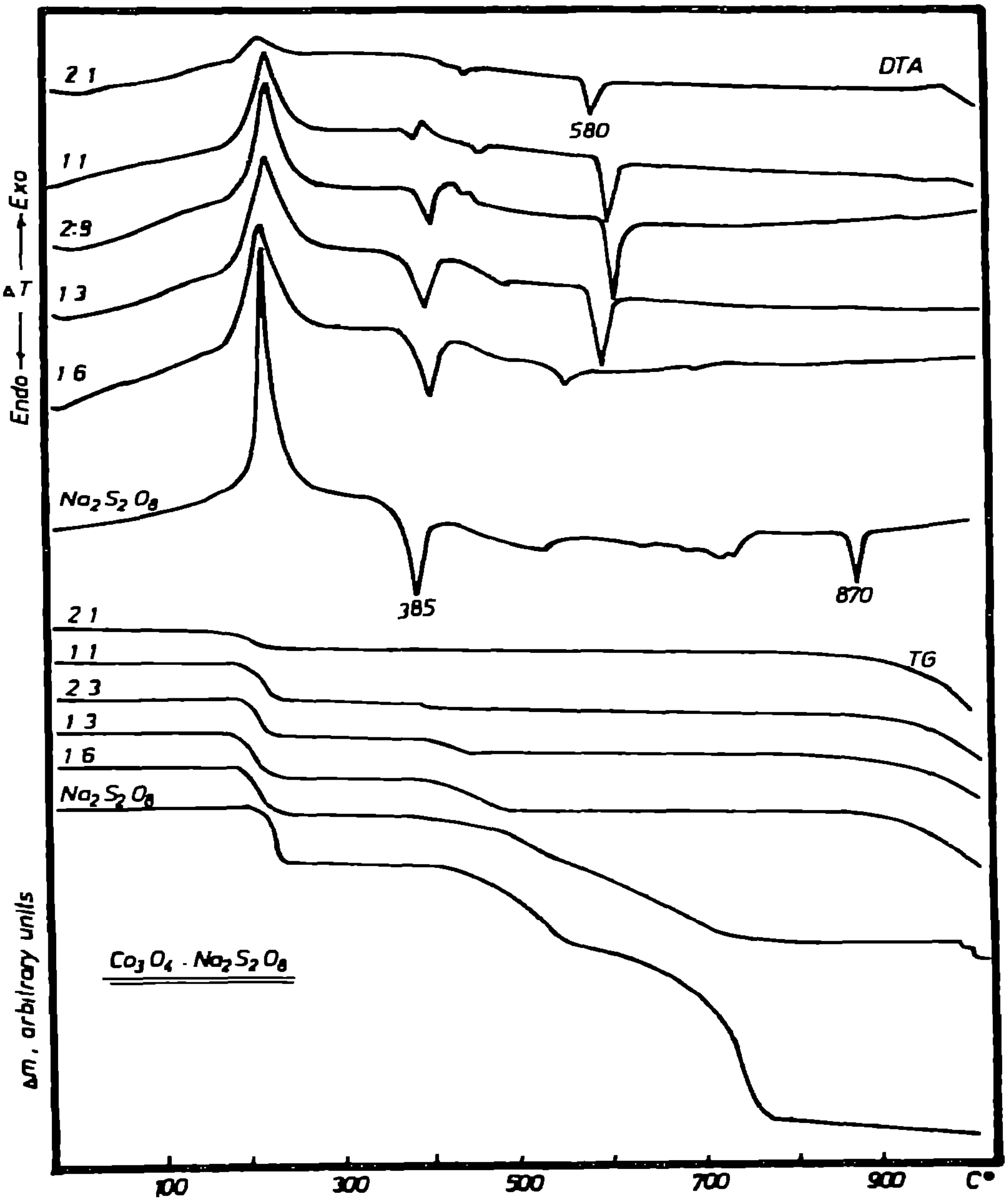

Fig. 1. TG and DTA curves of cobalt(II, III) oxide—sodium persulfate mixtures.

The TG curves also recorded weight loss caused by the escape of oxygen gas. From Table 1, it can be seen that, as the amount of the oxide increased, its effect increased and the temperature interval for its reaction became narrower. This is attributed to the catalytic effect of the oxide which accelerates the reaction.

Calculations obtained with 1 : 3 mole ratio showed that 84% of the $Na_2S_2O_7$ reacted with the oxide at 470°C and in the X-ray analysis of the sample isolated at this temperature, sharp lines were found at 6.13, 2.86 and

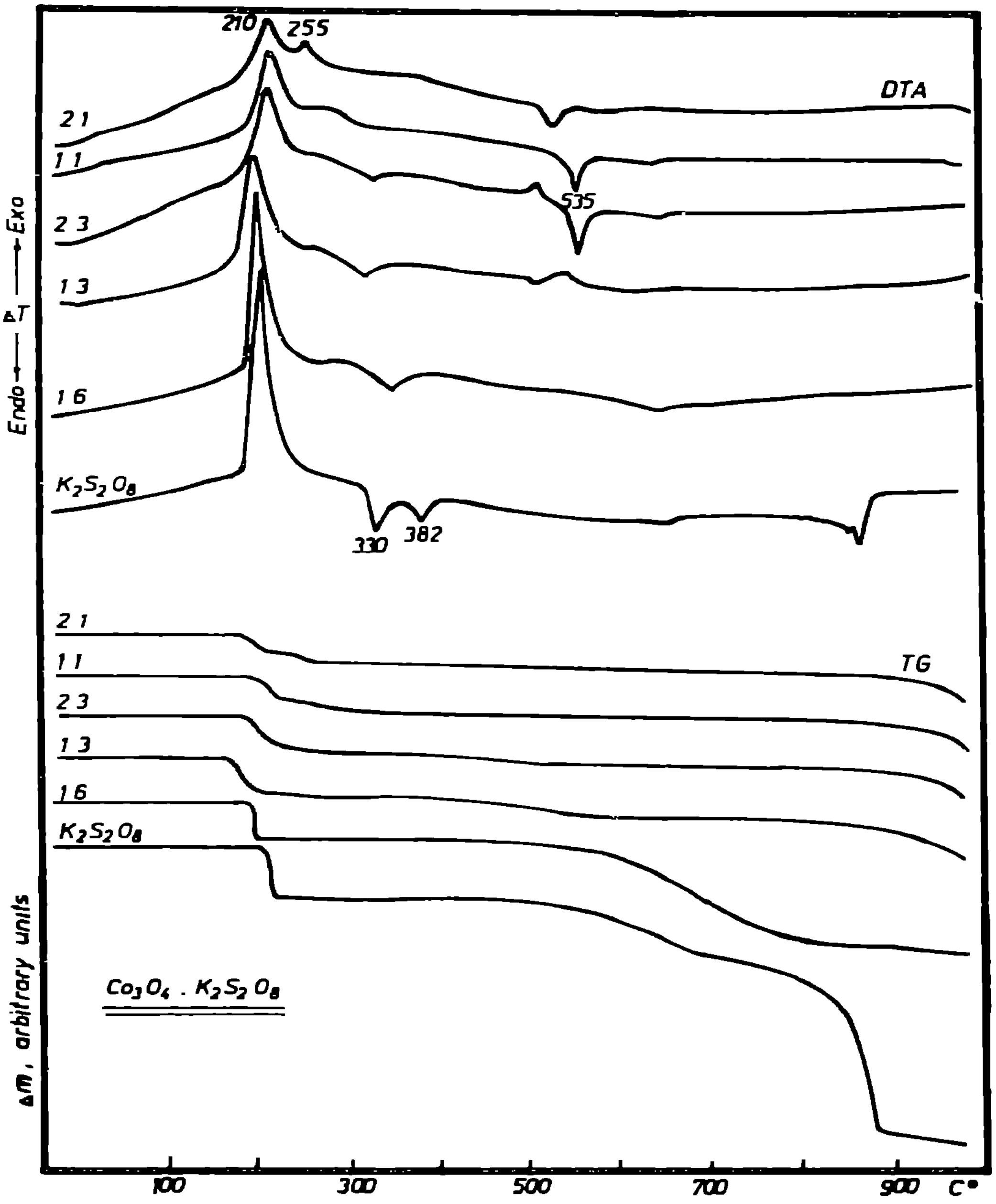

Fig. 2. TG and DTA curves of cobalt(II, III) oxide—potassium persulfate mixtures.

2.57 Å. The ASTM cards indicate that all three *d*-spacing values of the isolated sample correspond to sodium cobalt disulfate, $Na_2Co(SO_4)_2$. Furthermore, the largest sharp endotherm formed at 580°C on the DTA curve of the sample with a 1 : 3 mole ratio represents the melting point of this salt. Mole ratios other than 1 : 3 could not satisfy the conditions for the stoichiometric reaction

$$Co_3O_4 + 3\ Na_2S_2O_7 \rightarrow 3\ Na_2Co(SO_4)_2 + \frac{1}{2}O_2$$

TABLE 1

Amount of oxygen lost and temperature ranges for persulfate decomposition and oxide—pyrosulfate reaction in the Co_3O_4—$Na_2S_2O_8$ system at various mole ratios

Co_3O_4:$Na_2S_2O_8$	O_2 lost (mg)		Temp. range for $Na_2S_2O_8$ decomp. (°C)		Temp. range for oxide—$Na_2S_2O_7$ reaction (°C)		m.p. $Na_2Co(SO_4)_2$ (°C)
	Theoret.	Pract.	T_i	T_f	T_i	T_f	
0:1	13.4	13.4	185	220			
1:6	11.4	12.0	160	230	390	460	
1:3	10.0	10.5	160	225	382	470	580
2:3	8.0	9.0	160	210	375	430	575
1:1	6.6	9.0	150	220	370	440	575
2:1	4.4	4.5	160	210	210	440	580

TABLE 2

Amount of oxygen lost and temperature ranges for persulfate decomposition and oxide—pyrosulfate reaction in the Co_3O_4—$K_2S_2O_8$ system at various mole ratios

Co_3O_4:$K_2S_2O_8$	O_2 lost (mg)		Temp. range for $K_2S_2O_8$ decomp. (°C)		Temp. range for oxide—$K_2S_2O_7$ reaction (°C)		m.p. $K_2Co_2(SO_4)_3$ (°C)
	Theoret.	Pract.	T_i	T_f	T_i	T_f	
0:1	11.8	11.8	182	200			
1:6	10.3	10.0	160	180			
1:3	9.1	9.0	160	210	210	520	
2:3	7.4	7.0	165	210	210	500	540
1:1	6.2	6.0	165	210	210	295	535
2:1	4.2	4.2	160	210	210	255	535

All cobalt(III) ions of the oxide were reduced to cobalt(II) ions, leading to the formation of the compound $Na_2Co(SO_4)_2$. This reduction is attributed to the behaviour of the metal oxide at high temperature which tends to go to a lower valency state to form a more stable cation. This is confirmed by the ability of the high-valency cation Co(III) to accept electrons from electron-rich compounds, such as pyrosulfates $S_2O_7^{2-}$, and be reduced to a lower valency [8], and the typical behaviour of the P-type semiconductors, due to the presence of positive holes in the *d*-orbital, to accept electrons more than the others [9].

Potassium pyrosulfate, on the other hand, reacts with the oxide in the temperature range indicated in Table 2. Data obtained from the TG curves for samples isolated with 1 : 3 ratios at 320°C indicate that at least 89% of the pyrosulfate reacted with the oxide, a result which could not be duplicated by the other mole ratios used. This was confirmed by the X-ray examinations for the samples at 320°C which showed that the thermal product consisted of potassium cobalt trisulfate, $K_2Co_2(SO_4)_3$, and α-potassium sulfate, where the sharp lines at 2.64, 2.97, and 3.12 Å matched those for the trisulfate salt according to the ASTM cards.

The overall stoichiometric reaction could be expressed as

$$2\ Co_3O_4 + 6\ K_2S_2O_7 \rightarrow 3\ K_2Co_2(SO_4)_3 + 3\ K_2SO_4 + O_2$$

To the best of our knowledge, this solid state reaction is a new one for the preparation of trisulfate (see ref. 10). Moreover, the sharp endotherm that appeared on the DTA curve, Fig. 2, at 540°C for the sample with a 1 : 3 mole ratio could be regarded as the melting point of the deep purple coloured potassium cobalt trisulfate. This could be experimentally proved and reasoned as follows. Firstly, two samples were isolated from the 1 : 3 ratio sample at 320°C before the endotherm, and from the 2 : 3 ratio sample at 700°C after the endotherm. The first was found in a powdered crystalline state, while the second was found as a solidified melt. Secondly, this endotherm appeared in mixtures of all mole ratios at the same point, and there was a large temperature gap between its position and that of the melting point (1074°C) of the pure potassium sulfate. Therefore, this melting endotherm was proved not to be due to even a eutectic of K_2SO_4 and $K_2Co_2(SO_4)_3$.

Both salts, $Na_2Co(SO_4)_2$ and $K_2Co_2(SO_4)_3$, were thermally stable up to 800°C (Figs. 1 and 2), after which they decomposed gradually. This was shown by X-ray diffraction analysis taken for two samples of both salts isolated from the 2 : 3 mole ratio sample at 1020°C, where very large reductions in the intensities of the lines of these salts were detected and new lines for CoO appeared instead together with the line for the corresponding alkali metal sulfate. Their thermal degradations can be represented as

$$Na_2Co(SO_4)_2 \xrightarrow{\Delta} Na_2SO_4 + CoO + SO_3\uparrow$$

$$K_2Co_2(SO_4)_3 \xrightarrow{\Delta} K_2SO_4 + 2\ CoO + 2\ SO_3\uparrow$$

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