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EFFECTS OF NICKEL(II) OXIDE ON THE THERMAL DECOMPOSITION OF ALKALI PERSULFATES

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ABSTRACT

The thermal decomposition of $Na_2S_2O_8$ and $K_2S_2O_8$ has been studied derivatographically in the presence of NiO at various molar mixtures. Experiments have proved that the first decomposition stage (persulfate into pyrosulfate) is independent of the amount of the oxide present. During the second decomposition stage (pyrosulfate into sulfate) which occurs in the melt, NiO plays the role of lowering the melting, the initial and final decomposition temperatures of pyrosulfates. The lowest melting temperatures recorded for $Na_2S_2O_8$ and $K_2S_2O_8$ are 320 and 280°C, respectively.

A mechanism has been proposed to describe the catalytic action of NiO on the thermal decomposition of alkali pyrosulfates. The mechanism makes use of the semiconductivity of NiO and the availability of electron-rich centers in the pyrosulfate group to help the formation of an adsorption complex between them.

NiO reacts to some extent with alkali pyrosulfates forming the yellow $NiSO_4$ and alkali sulfates as separate products.

NiO and $NiSO_4$ form eutectic mixtures with alkali sulfates melting at temperatures lower than those of the pure salts.

INTRODUCTION

Transition metal oxides show semiconductivity due to non-stoichiometric defects in the crystal lattice. These defects may occur because of the ability of the metal to exist in more than one oxidation state or the ability of the oxide to lose oxygen when heated to higher temperatures[1]. Falicov and Koiller[2] have given an interpretation for the semiconductivity of transition metal oxides in terms of a model, which involves itinerant metallic *s*-electrons, oxygen *p*-electrons, and localized highly correlated transition metal *d*-electrons. Their activity of catalyzing the thermal decomposition of potassium permanganate helped in establishing a mechanism for this decomposition as a charge transfer reaction between identical anions[3]. Rudloff and Freeman[4] have studied the catalytic effect of fourteen metal oxides on the thermal decomposition of potassium chlorate and potassium perchlorate and suggested a mechanism for the decomposition of potassium chlorate. In this mechanism, a surface adsorption complex may be formed between the bimolecular anions and the semiconductor. The complex then disproportionates into more stable species forming the decomposition products together with the semiconductor at lower temperatures. Udupa[5, 6] has studied the action of mixtures of nickel(II) oxide and chromium trioxide as well as their double oxide, nickel chromite $NiCr_2O_4$, on the thermal decomposition of potassium chlorate and potassium perchlorate. The catalytic activity of ferric oxide on the decomposition of potassium perchlorate was shown to depend on the method of preparation of the oxide[7].

In the present work the thermal decomposition of sodium and potassium persulfates which was already studied individually[8], is investigated in the presence of the *p*-type semiconductive nickel(II) oxide in mixtures of varying molar ratios.

EXPERIMENTAL

Materials

$Na_2S_2O_8$ and $K_2S_2O_8$ were analytical grade (Hopkin & Williams). NiO was prepared by the thermal decomposition of analytical grade nickel(II) nitrate[9] and kept dry.

The calculated amounts of nickel(II) oxide and the persulfate were mixed and powdered in an agate mortar for 15 min and kept at 80°C for 20 min. This was followed immediately by simultaneous thermogravimetry (TG) differential thermogravimetry (DTG) and differential thermal analysis (DTA) of the samples between 20°C and 1000°C.

The apparatus and general procedure have been described earlier[8].

RESULTS AND DISCUSSION

In Figs. 1 and 2 the TG and DTA curves are plotted against temperature for the decomposition of sodium and potassium persulfates in intimate admixture with nickel oxide–persulfate mole ratios of 1:4, 1:2, 1:1, 2:1, and 4:1. The lowering in the melting temperature, the initial decomposition temperature, and the temperatures at 50 and 100% of decomposition, of sodium and potassium pyrosulfates due to increasing proportions of nickel(II) oxide are shown in Tables 1 and 2.

Figures 1 and 2 indicate that the decomposition of the persulfate into pyrosulfate is independent of the amount of the oxide present.

From the analysis of TG plots, it appears that for a mole ratio x, where $1:4 \leqslant x \leqslant 2:1$, a constant amount of SO_3, equivalent to a quarter of a mole of the gas fails to escape and reacts with nickel oxide forming the yellow anhydrous nickel(II) sulfate, $NiSO_4$, as being detected by the X-ray diffraction patterns of the cooled products. An equation can, therefore, be given for the reaction of nickel(II) oxide with molten alkali pyrosulphate as follows

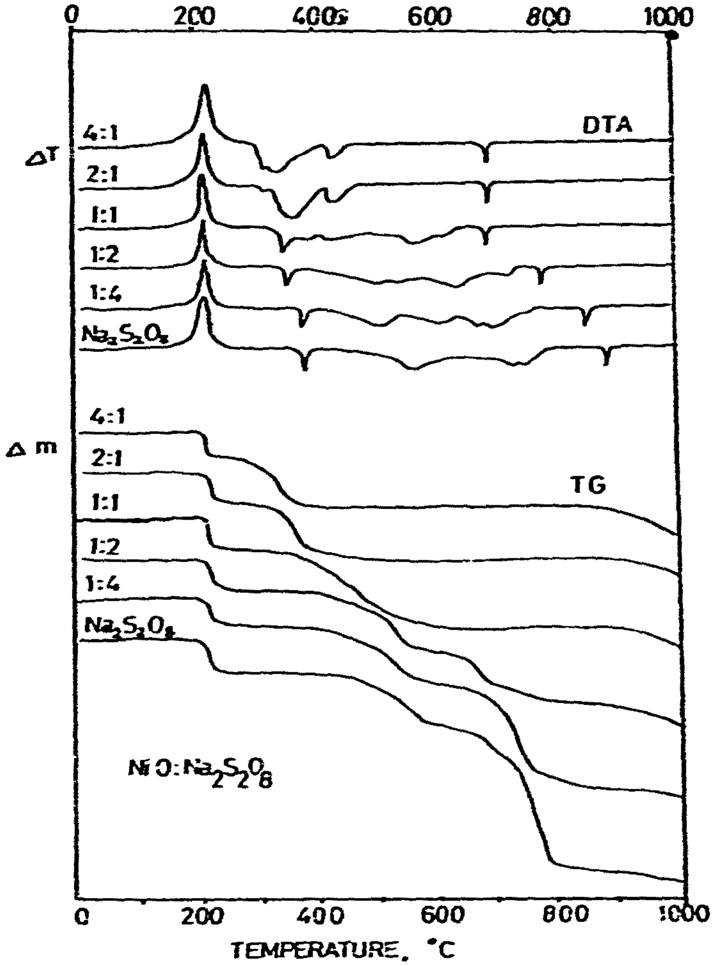


Fig. 1. TG and DTA curves of NiO: $Na_2S_2O_8$ mixtures at molar ratios of 1:4, 1:2, 1:1, 2:1, and 4:1, respectively.

$$\frac{1}{4}NiO + nM_2S_2O_7 \xrightarrow{\theta} \frac{1}{4}NiSO_4 + nM_2SO_4 + (n-\frac{1}{4})\,SO_3 \qquad (I)$$

The above reaction would, consequently, provide an explanation for the weak catalytic effect of nickel(II) oxide at 1:8 and 1:4 mole ratios.

The melting points of $Na_2S_2O_7$ and $K_2S_2O_7$ decrease as the amount of nickel(II) oxide increases. Melting temperatures of 332 and 280°C were recorded for sodium and potassium pyrosulfates, respectively, at 1:1 mole ratio. However, in mixtures of 2:1 and 4:1 the melting endotherms at the DTA curves were embedded in the bigger endotherm corresponding to the decomposition of the pyrosulfate, which already begins in the solid state.

The melting points of sodium and potassium sulphates are also affected by the amount of nickel(II) oxide and nickel(II) sulfate present. The latter may form eutectic mixtures with alkali sulfates melting at temperatures lower than the melting points

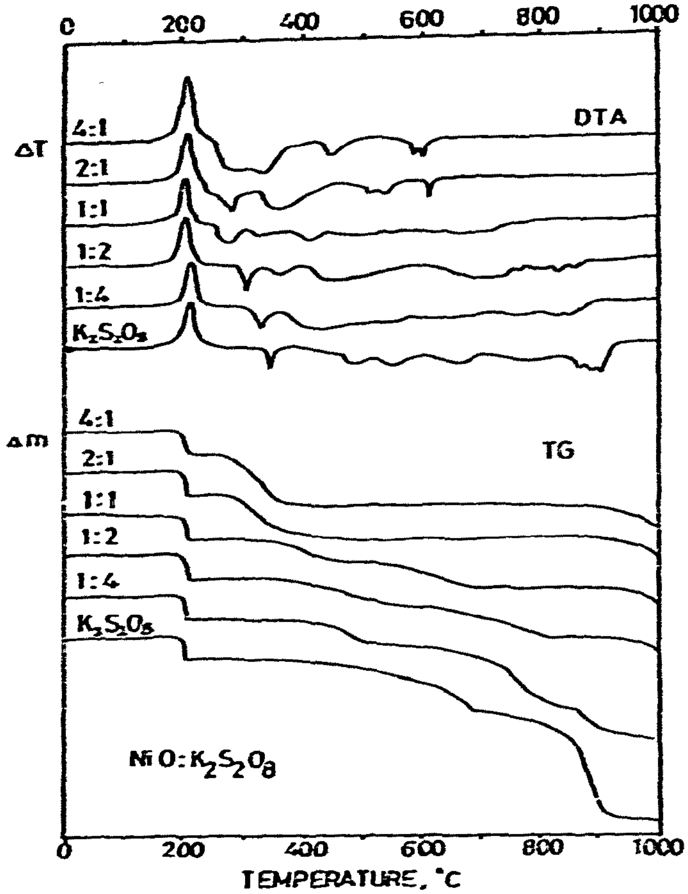


Fig. 2. TG and DTA curves of NiO: $K_2S_2O_8$ mixtures at molar ratios of 1:4, 1:2, 1:1, 2:1, and 4:1, respectively.

TABLE I

THE TEMPERATURES OBTAINED FOR THE DECOMPOSITION OF SODIUM PYROSULFATE IN THE PRESENCE OF NICKEL(II) OXIDE

NiO:$Na_2S_2O_8$ mole ratio	*m.p.*	t_i[a]	$t_{50\%}$[b]	$t_{100\%}$[c]
1:4	380	380	650	780
1:2	360	352	540	760
1:1	332	300	475	610
2:1	320	312	360	500
4:1	—[d]	252	328	440
$Na_2S_2O_8$ only	380	380	698	790

[a] Initial decomposition temperature. [b] Temperature at 50% of decomposition. [c] Final decomposition temperature. [d] The melting point was not clearly determined since the melting endotherm was embedded within the decomposition endotherm.

TABLE 2

THE TEMPERATURES OBTAINED FOR THE DECOMPOSITION OF POTASSIUM PYROSULFATE IN THE PRESENCE OF NICKEL(II) OXIDE

NiO:$K_2S_2O_7$ mole ratio	*m.p.*	t_i[a]	$t_{50\%}$[b]	$t_{100\%}$[c]
1:4	312	386	735	920
1:2	306	315	700	900
1:1	280	305	554	742
2:1	—[d]	297	352	575
4:1	—[d]	250	315	500
$K_2S_2O_7$ only	340	390	740	920

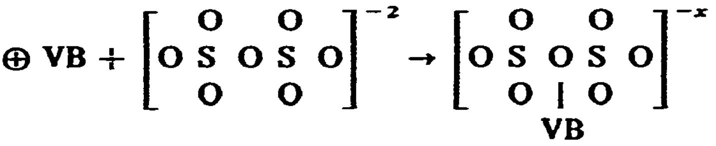
[a] Initial decomposition temperature. [b] Temperature at 50% of decomposition. [c] Final decomposition temperature. [d] The melting point was not clearly defined, since the melting endotherm was embedded within the decomposition endotherm.

of the individual sulfates. The lowest melting temperatures obtained for sodium and potassium sulfates are 680 and 597°C, respectively.

Above 840°C the TG curves move downwards to indicate the decomposition of nickel(II) sulfate into nickel(II) oxide and sulfur trioxide[10].

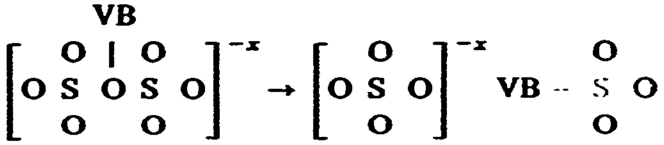
On the basis of the Rudloff-Freeman mechanism of the catalytic decomposition of potassium chlorate[4], the following mechanism has been proposed for the decomposition of alkali pyrosulfates being catalyzed by the semiconductive nickel(II) oxide:

The pyrosulfate anion adsorbs on the surface of the semiconductive oxide with a partial and/or total electron transfer to the positive hole in the valence band (VB) and forms the surface complex



$$\oplus\,\mathrm{VB} + \left[\begin{array}{ccccc} & O & & O & \\ O & S & O & S & O \\ & O & & O & \end{array}\right]^{-2} \rightarrow \underset{\mathrm{VB}}{\left[\begin{array}{ccccc} & O & & O & \\ O & S & O & S & O \\ & O & | & O & \end{array}\right]^{-x}} \qquad (x < 2) \qquad (2)$$

consequently the bond between the central oxygen atom and adjacent sulfur atom of the anion becomes less stable and disproportionation occurs at a much lower temperature than that in the absence of the catalyst,



$$\overset{\mathrm{VB}}{\left[\begin{array}{ccccc} & O & | & O & \\ O & S & O & S & O \\ & O & & O & \end{array}\right]^{-x}} \rightarrow \left[\begin{array}{ccc} & O & \\ O & S & O \\ & O & \end{array}\right]^{-x} \quad \mathrm{VB} - \begin{array}{c} O \\ S\;O \\ O \end{array} \qquad (3)$$

consequently the adsorbed, rather unstable $[SO_4\ VB]^{-x}$ surface anion further decomposes into SO_4^{2-} as the most stable anion taking up along the electron partially donated to the valence band of the semiconductor.

This mechanism suggests, however, that the decomposition of the pyrosulfate is unimolecular, i.e., only one pyrosulfate anion is involved, and that the central oxygen atom is the most available part of the anion with two lone pairs of electrons ready to be shared with the positive hole of the semiconductor. The other oxygen atoms, however, are bound to the sulfur atom through bonds with partial double character. Thus the number of electrons available to be shared with the valence band of the semiconductor will be less than in the case of the central oxygen atom.

The DTA curves of nickel(II) oxide mixtures with sodium and potassium persulfates indicate that the oxide reacts with sodium pyrosulfate between 427 and 460°C and with potassium salt between 440 and 470°C forming the nickel(II) sulfate together with the sodium and potassium sulfates, respectively (Figs. 1 and 2). This property of nickel(II) oxide makes it efficient to act as a semiconductor more than being a chemically reactive species below these temperature ranges.

At 592°C, an endothermic peak is recorded at the DTA curves of the higher mole ratios of $NiO:K_2S_2O_8$ (Fig. 2) other than the melting endotherm following it, corresponding to the α, β phase transition of potassium sulfate[11]. From this it is evident, that only individual sulfates are formed as the major products of such treatment and not the double salts named alkali–nickel sulfates.

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