CATALYTIC EFFECTS OF COPPER(II) OXIDE AND ZINC(II) OXIDE ON THE THERMAL TRANSITIONS OF SODIUM AND POTASSIUM PERSULFATES

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The thermal transitions of Na₂S₂O₈ and K₂S₂O₈ have been studied by means of a derivatograph in the presence of CuO or ZnO at various molar mixtures. A slight shift in the DTG peak of the first decomposition stage (persulfate into pyrosulfate) to higher temperature was noticed as the amount of oxide increases.

The second decomposition stage (pyrosulfate into sulfate) was shown to proceed via the formation of double salts of alkali metal copper(II) sulfates and alkali metal zinc(II) sulfates, namely, Na₂Cu(SO₄)₂, K₂Cu(SO₄)₂, Na₂Zn(SO₄)₂ and K₂Zn(SO₄)₂. The reaction has a close relation to the semiconductivity of both oxides. The melting points recorded for these double salts were respectively 532, 634, 467 and 462°.

The results were confirmed by the IR spectra of the reaction products.

The double salts slowly decompose into the metal oxide, alkali metal sulfates, and sulfur trioxide.

In a study of the interaction of metal oxides with the alkali metal persulfates and their decomposition products, it was shown [1] that nickel(II) oxide catalyzes the thermal decomposition of alkali metal pyrosulfates into the sulfates, and a mechanism was proposed for this catalytic decomposition. The mechanism was based essentially on the semiconductive behaviour of this oxide and its adsorptive characteristics towards the pyrosulfate anions. Titanium (IV) oxide, on the other hand, was shown to react with the persulfates and the pyrosulfates at high temperatures, forming products of a complex nature [2].

In the present work, the derivatograph (TG, DTG and DTA) is applied to the study of the thermal behaviour of alkali metal persulfates in the presence of copper (II) oxide or zinc(II) oxide at various molar ratios within the temperature range 20–1000°. The possibility of double salt formation is also discussed.

Experimental

Materials

All the chemicals used were analytical grade Na₂S₂O₈ and K₂S₂O₈ were Hopkin and Williams AnalaR; CuO and ZnO were BDH AnalaR products.

Apparatus and methods

The present investigation comprised experiments on TG, DTG and DTA methods. The apparatus and techniques were described earlier [1].
The infrared spectra were obtained using the Pye-Unicam SP-1100 I.R. spectrophotometer. The samples were analyzed as KBr discs.

Results and discussion

CuO + M₂S₂O₈ mixtures

In Figs 1 and 2 the TG and DTA curves are plotted against temperature for sodium and potassium persulfates in intimate admixtures with copper(II) oxide, in oxide to persulfate molar ratios of 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 4 : 1.

A slight shift in the DTG peak temperatures of the decomposition of the alkali metal persulfates to higher values is obtained with the increased proportion of the oxide in the mixture. This may be due mainly to dilution effects [3] since the persulfate decomposition reactions are second-order reactions [4, 5].

![Graph showing TG and DTA curves](image)

Fig. 1. TG and DTA curves of CuO : Na₂S₂O₈ mixtures at mole ratios 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 4 : 1 respectively

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