

Short Communication

REACTION BETWEEN CHROMIUM(III) OXIDE AND OXYGEN IN THE PRESENCE OF SODIUM CARBONATE

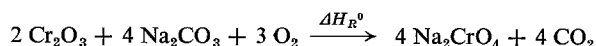
A DTA STUDY

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The large scale manufacture of sodium chromate is carried out by heating finely ground chromite ore mixed with sodium carbonate and lime in air. The essential reaction leading to the formation of sodium chromate is



We describe in this brief communication our preliminary studies on this reaction by differential thermal analysis to establish the temperature and degree of chromate formation.

Experimental

Chromium(III) oxide was prepared by heating analytical grade ammonium dichromate and anhydrous sodium carbonate of Analar grade.

The differential thermal analysis curves were obtained on a Rigaku-Denki Modular (Thermoflex) Thermal Analysis system using ~10 mg quantities of finely ground samples containing varying proportions of chromium(III) oxide and sodium carbonate. The heating rate was 10°/min and all samples were heated in a static air or dynamic nitrogen atmosphere. Infrared spectra were taken on a Perkin-Elmer Model 457 Spectrophotometer using the KBr pellet technique. X-ray powder patterns were obtained on a Unicam X-ray diffractometer using nickel filtered CuK_α radiation and a powder camera of 57.3 mm radius. Absorption and diffuse reflectance spectra were taken on a Unicam SP800 recording Spectrophotometer.

Results and discussion

The DTA profiles of the samples containing varying proportions of chromium(III) oxide and Na_2CO_3 are given in Fig. 1. The reaction is marked by an endothermic peak as is to be expected on thermodynamic considerations, since

ΔH_R^0 is approximately $+18 \text{ kcal mol}^{-1} \text{ Cr}_2\text{O}_3$ at 298 K. The conversion of chromium(III) oxide to sodium chromate is quantitative at $\text{Na}_2\text{CO}_3/\text{Cr}_2\text{O}_3$ molar ratios of 2 : 1 or greater. The following were further observations:

(1) No reaction occurs when air is excluded (thermal analysis was carried out using a dynamic nitrogen atmosphere).

(2) With mixtures containing sodium carbonate/ Cr_2O_3 molar ratios exceeding 2 : 1 the reaction occurs at 672° , but for molar ratios less than 2 : 1, the reaction temperature is 780° . It appears that excess sodium carbonate reduces the temperature of reaction.

(3) The reaction product formed at $\text{Na}_2\text{CO}_3/\text{Cr}_2\text{O}_3$ mole ratios of less than 2 : 1 was an orange-yellow solid contaminated with unreacted Cr_2O_3 . As the proportion

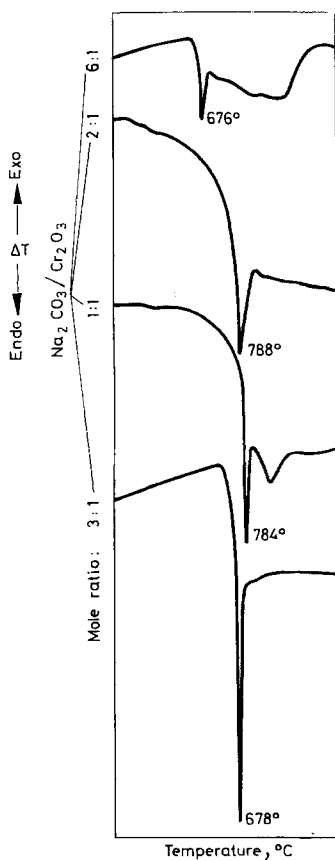


Fig. 1. DTA profiles of molten $\text{Na}_2\text{CO}_3/\text{Cr}_2\text{O}_3$ mixtures

of sodium carbonate in the reaction mixture increased, the reaction proceeded to completion and the product was pure yellow sodium chromate.

Wadier [2] reported that in the reaction between chromic oxide and alkali metal nitrates, dichromate is formed with reactant mixtures of $\text{MNO}_3/\text{Cr}_2\text{O}_3$ mole ratios less than 4 : 1, whereas with a higher proportion of chromic oxide, the reaction product consists of a chromate/dichromate mixture. Further, the temperature of the reaction, as indicated by a sharp DTA endotherm between 600 and 800°, depends on the particular alkali metal molten solvent and decreases as the $\text{MNO}_3/\text{Cr}_2\text{O}_3$ mole ratio decreases.

Udupa [3] examined the decomposition of potassium nitrate/chromium(III) oxide mixtures by TG/DTA and found that with $\text{KNO}_3/\text{Cr}_2\text{O}_3$ mole ratios of 2 : 1 or less, the reaction was incomplete and the product was dichromate. As the $\text{KNO}_3/\text{Cr}_2\text{O}_3$ mole ratio increased, the degree of reaction increased and chromate was formed quantitatively when the $\text{KNO}_3/\text{Cr}_2\text{O}_3$ mole ratio exceeded 5 : 1.

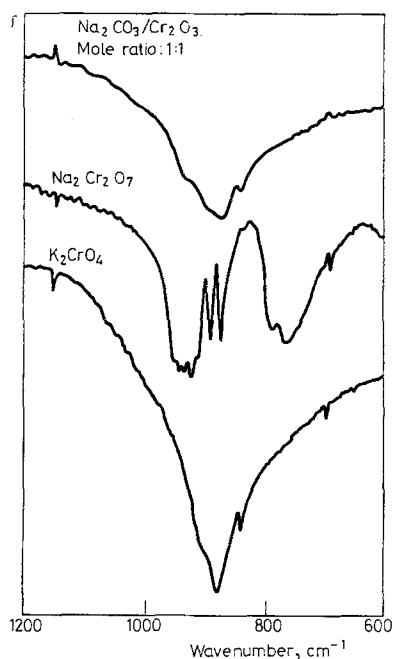


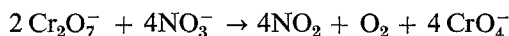
Fig. 2. Infrared spectra of 1 : 1 mole ratio $\text{Na}_2\text{CO}_3/\text{Cr}_2\text{O}_3$, sodium dichromate and potassium chromate

Brown and Ferguson [4] examined the oxidation of chromium(III) in silica/sodium carbonate molten solvent by TG/DTA. A $\text{SiO}_2/\text{Na}_2\text{CO}_3/\text{Cr}_2\text{O}_3$ reactant mixture of 1 : 1 : 2 mole ratio yielded only sodium chromate as product at 785°.

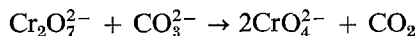
We examined the orange-yellow product derived from thermal analysis of $\text{Na}_2\text{CO}_3/\text{Cr}_2\text{O}_3$ reactant mixtures of mole ratio less than 2 : 1 by X-ray diffraction powder photography and infrared, (Fig. 2) diffuse reflectance and UV-visible

absorption spectrophotometry and found no evidence for the presence of dichromate despite the orange-yellow colour of the sample. All our analytical data confirm the presence of chromate.

It is interesting to note that the role of the molten solvent in chromium(III) oxidation reactions is uncertain. However Duke and Iverson [5] have shown that the acid-base reaction



proceeds in fused $\text{KNO}_3/\text{NaNO}_3$ eutectic at 250° which explains the observation of Udupa [3] that mixtures of $\text{KNO}_3/\text{Cr}_2\text{O}_3$ with nitrate in excess yielded only chromate. Shams El Din and Gerges [6] have provided potentiometric titration data which confirm reaction between dichromate ion and carbonate ion in fused potassium carbonate to yield chromate according to the reaction



Thus it appears that dichromate is unstable in molten basic solvents and our thermal and analytical data and that of Brown and Ferguson [4] provide additional evidence for the exclusive stability of chromate in these solvents.

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