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Note

Thermal decomposition of potassium nitrite in the presence of chromium(III) oxide

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The studies on the thermal behaviour of intimate mixtures of Cr_2O_3 and oxidants such as $KClO_4$[1], $KClO_3$[2] and KNO_3[3] revealed that chromium(III) oxide not only lowers the decomposition temperatures of the pure salts but also chemically interacts and is oxidized into the hexavalent state. The purpose of the present study is to find out the influence of Cr_2O_3 on the decomposition of KNO_2 and to see whether KNO_2 could oxidize Cr(III) to the hexavalent state. Potassium nitrite melts at 298°C and decomposes above 650°C. In this paper is reported the investigation made on the thermal decomposition of different molar ratios of KNO_2 and Cr_2O_3 in air employing thermogravimetry and differential thermal analysis. The decomposition products are examined by chemical analysis and infrared spectral measurements.

EXPERIMENTAL

Chromium(III) oxide was prepared by heating reagent grade $Cr(NO_3)_3 \cdot 9H_2O$ to 600°C. Commercially available potassium nitrite was recrystallized and used. All other reagents employed were analytical reagent grade.

Mixtures of KNO_2 and Cr_2O_3 were prepared in 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 8:1 and 10:1 molar ratios by taking the required amounts in an agate mortar and grinding for 10–15 min.

The thermogravimetric analyses were made in air using Stanton HT-SM recording thermobalance at a linear heating rate of 6°C per min with 200 mg samples in platinum crucible containers. Differential thermal analyses were made in air using Netzsch differential thermal analyzer. About 100–150 mg samples were taken for each run with standard alumina as reference material. Muffle furnace whose temperature could be controlled with an accuracy of ±10°C was used to heat the mixtures for characterization of the decomposition products. Infrared spectra were measured on Perkin-Elmer 257 and Beckman IR 12 spectrophotometers using KBr pellet and Nujol mull techniques.

Chromium(VI) in the decomposition products was determined by the iodometric method[4] after destroying the excess KNO_2 if any by treating with sulphamic acid.

RESULTS AND DISCUSSION

Thermogravimetric curves of nine different molar ratios of KNO_2 and Cr_2O_3 are plotted in Fig. 1. The curves indicate that the decomposition of KNO_2 in the mixtures sets in at 400°C. The decomposition is complete for 1:2, 1:1, 2:1, 3:1, 4:1, 5:1 and 6:1 molar ratios by 600°C. For the molar ratios 8:1 and 10:1, the weight loss continues upto 750°C. Free KNO_2 is found to decompose above 650°C suggesting that Cr_2O_3 lowers the decomposition temperature of pure KNO_2.

The DTA plots of different mixtures are identical and the plots of 4:1, 6:1 and 8:1 molar ratios of KNO_2 and Cr_2O_3 are given in Fig. 2. The endotherm at 300°C is ascribed to the melting of KNO_2 and an exotherm at 400°C is due to the oxidation of Cr(III) to Cr(VI). The endotherm at 160°C reappears as an exotherm around

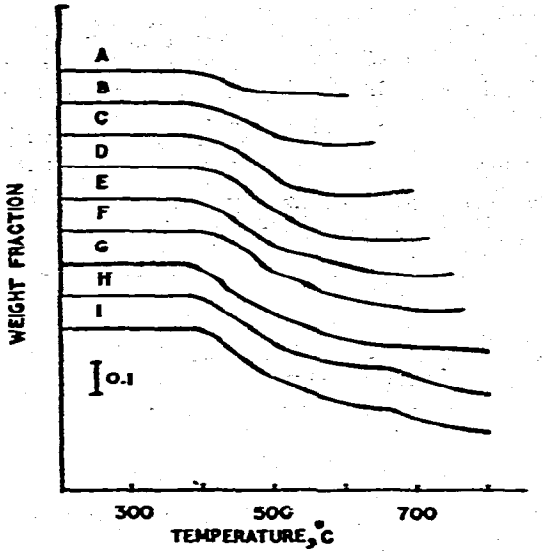

Fig. 1. TG plots of 1:2(A), 1:1(B), 2:1(C), 3:1(D), 4:1(E), 5:1(F), 6:1(G), 8:1(H) and 10:1(I) molar ratios of KNO_2 and Cr_2O_3.

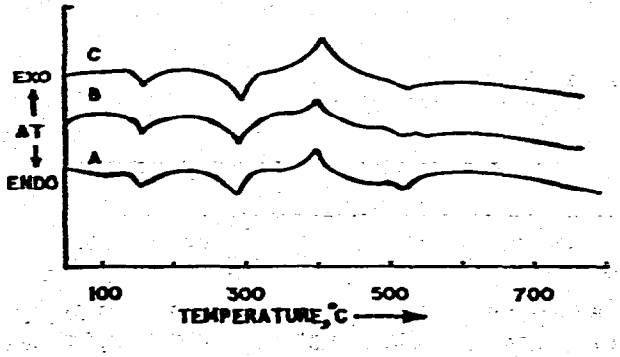

Fig. 2. DTA plots of 4:1(A), 6:1(B) and 8:1(C) molar ratios of KNO_2 and Cr_2O_3

150°C when free KNO_2 and various KNO_2–Cr_2O_3 mixtures are heated to 300°C and cooled to 100°C, suggesting the effect may be due to the crystallographic phase transformation. However, this has to be confirmed by high-temperature powder diffraction patterns. The small endothermic hump at 500°C is probably associated with the decomposition of KNO_2.

The characterization of the decomposition products was made by heating the different mixtures at 700°C for 15 min in a muffle furnace. The products are found to be hygroscopic and the aqueous solutions to be alkaline. The residues of 1:2, 1:1, 2:1, 3:1, 4:1, and 5:1 mixtures are partly soluble in water whereas those of 6:1, 8:1 and 10:1 are disinctly yellow in colour and are completely soluble in water. The analytical results for Cr(VI) content in the residues are given in Table 1. It is clear from the results that Cr(III) is completely oxidized into Cr(VI) when the molar ratio of KNO_2 to Cr_2O_3 is equal to and greater than six.

In order to identify the oxidized products the decomposition residues are subjected to infrared spectral analysis. The spectra of the residues of 1:2, 1:1, 2:1, 3:1, 4:1 and 5:1 showed absorptions at (cm^{-1}) 410w, 440w, 560m and 620s characteristic of Cr_2O_3[5] and at 386w, 400w, 870s and 1240w due to K_2CrO_4[6,7]. The residues of 6:1, 8:1 and 10:1 molar ratios exhibited the infrared bands characterisic of K_2CrO_4 only. The hygroscopic nature of the residues and the alkalinity of their aqueous solution suggest the presence of potassium oxide.

TABLE 1

ANALYTICAL DATA ON THE DECOMPOSITION PRODUCTS OF POTASSIUM NITRITE AND CHROMIUM(III) OXIDE MIXTURES

	KNO_2:Cr_2O_3								
	1:2	1:1	2:1	3:1	4:1	5:1	6:1	8:1	10:1
Chromium(VI) Found (%)	4.6	7.3	10.7	12.7	14.0	15.0	15.6	12.3	10.3
Extent of Cr(III) Oxidation (%)	8.6	16.6	33.2	49.6	66.5	82.8	99.6	98.5	98.2

TABLE 2

THERMOGRAVIMETRIC DATA ON THE DECOMPOSITION OF DIFFERENT MOLAR RATIOS OF POTASSIUM NITRITE AND CHROMIUM(III) OXIDE

Weight loss (wt. %)	KNO_2:Cr_2O_3								
	1:2	1:1	2:1	3:1	4:1	5:1	6:1	8:1	10:1
Found	7.5	12.5	18.5	22.0	24.0	26.0	27.0	30.5	33.0
Calc.	7.7	12.7	18.6	22.1	24.4	26.0	27.2	30.7	33.1

The thermogravimetric results of the different mixtures are given in Table 2. These results together with the extent of Cr(III) oxidation from the analytical data (Table 1) suggest the following overall reaction scheme for the oxidation of Cr_2O_3 by KNO_2.

$$x\,KNO_2 + Cr_2O_3 \rightarrow x/3\,K_2CrO_4 + x/6\,K_2O + x\,NO + (1 - x/6)\,Cr_2O_3 \ldots x = 1,2, \ldots 6$$

$$y\,KNO_2 + Cr_2O_3 \rightarrow 2K_2CrO_4 + (y/2 - 2)\,K_2O + y\,NO + (y-6)/4\,O_2 \ldots y \geqslant 6$$

$$KNO_2 + z\,Cr_2O_3 \rightarrow 1/3\,K_2CrO_4 + 1/6\,K_2O + NO + (z\text{-}1/6)\,Cr_2O_3 \ldots z \geqslant 2$$

From the reaction scheme it is clear that Cr(III) abstracts oxygen from the nitrite moiety and gives nitric oxide which combines with the oxygen in the air to form nitrogen dioxide as evidenced by the liberation of the brown fumes during the decomposition.

It is interesting to note that $K_2Cr_2O_7$ is one of the oxidized products[3] during the decomposition of limited amounts of KNO_3 and Cr_2O_3 mixtures whereas K_2CrO_4 is the only oxidized product formed with KNO_2–Cr_2O_3 mixtures.

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