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THERMAL DECOMPOSITION OF POTASSIUM NITRATE IN THE PRESENCE OF CHROMIUM(III) OXIDE

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ABSTRACT

Thermal decomposition studies of intimate mixtures of different molar ratios of potassium nitrate and chromium(III) oxide were made by employing thermogravimetry, differential thermal analysis, chemical analysis, infrared spectral measurements and X-ray powder diffraction patterns. Potassium nitrate in the presence of chromium(III) oxide starts decomposing around 350°C which is much below the decomposition temperature of pure potassium nitrate. Chromium(III) is completely oxidized into its hexavalent state when the mole ratio of KNO_3 to Cr_2O_3 is greater than three.

INTRODUCTION

The thermal behaviour of potassium nitrate has been studied by several investigators[1–3] and it is found that it undergoes a phase transformation at 130°C followed by melting around 330°C. The decomposition of KNO_3 takes place around 730°C giving nitrous oxides as volatile products. Recently, we have studied the oxidation of chromium(III) during the decomposition of intimate mixtures of $KClO_4$ and Cr_2O_3[4], and $KClO_3$ and Cr_2O_3[5]. The aim of the present investigation is to investigate the influence of Cr_2O_3 on the decomposition of KNO_3 and to see whether KNO_3 could oxidize Cr(III) to its hexavalent state. In this paper are reported the studies made on the decomposition of different molar ratios of KNO_3 and Cr_2O_3 in air employing thermogravimetry and differential thermal analysis. The decomposition products are examined by chemical analysis, infrared spectral measurements and X-ray powder diffraction patterns.

EXPERIMENTAL

Materials

Chromium(III) oxide was prepared by heating AnalaR CrO_3 at 600°C for 2 h. Commercially available potassium nitrate was used after recrystallization. All other reagents employed were analytically pure grade.

Methods

Mixtures of KNO_3 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 and grinding in an agate mortar for 15–20 min.

The thermogravimetric studies were made in air using a Stanton recording thermobalance at a linear heating rate of 6°C min^{-1} with 100 mg samples in platinum crucible containers. Differential thermal analyses were made in air using a Netzsch differential thermal analyzer. About 60–100 mg samples were taken for each run with inert alumina as reference material. The heating rate of the furnace was adjusted to 10°C per min^{-1}.

Infrared spectra were measured on Perkin-Elmer 257 and Beckman IR 12 spectrophotometers using KBr pellet and Nujol mull techniques.

X-ray powder diffraction patterns were taken with a Philips X-ray generator using CuK_α radiation and a 114.6 mm diameter Debye–Scherrer camera.

Analytical

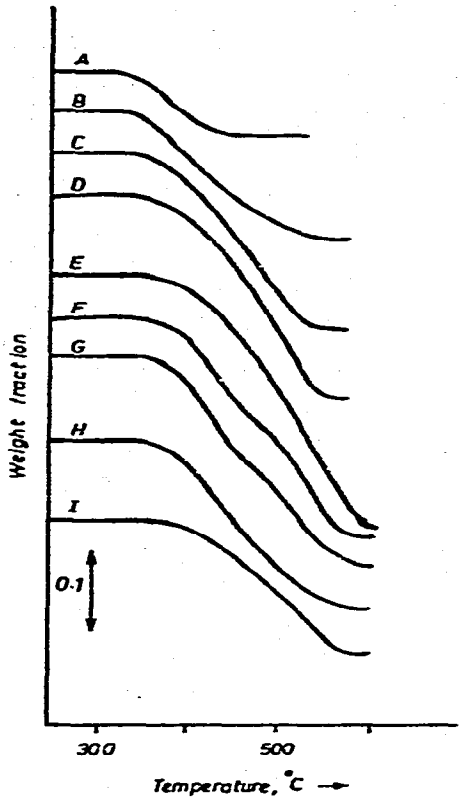
Chromium(VI) in the decomposition products was determined by the iodometric method.

RESULTS AND DISCUSSION

The thermogravimetric plots of nine different molar ratios of KNO_3 and Cr_2O_3 are given in Fig. 1. The curves suggest that the decomposition of KNO_3 in the mixtures takes place in the temperature range 350–600°C. When pure KNO_3 is heated under identical conditions, it is observed that there is no weight change in this temperature range. However, it is known[2] that decomposition of KNO_3 begins at about 730°C. The results suggest that Cr_2O_3 lowers the decomposition temperature of pure KNO_3.

The DTA plots of different mixtures are similar and gave three endotherms when heated to 600°C. The plots of 1:1, 3:1 and 6:1 molar ratios are given in Fig. 2 as representives. The endotherm at 130°C is assigned[1] to the crystallographic phase transformation of KNO_3 from room temperature orthorhombic to rhombohedral form. The endotherm at 330°C is attributed to the melting of KNO_3 and the one around 500°C to its decomposition.

The decomposition residues of 1:2, 1:1 and 2:1 are partly soluble in water giving yellow solutions and the insoluble part was found to be unreacted Cr_2O_3. The decomposition products of other mixtures are completely soluble in water. The aqueous solutions of all residues are found to be alkaline. The residues of 6:1, 8:1 and 10:1 molar ratios are distinctly yellow in colour whereas those of 3:1, 4:1 and 5:1 are yellow-orange. The residues of decomposition are found to absorb water vapour from the atmosphere with time. The analytical results for Cr(VI) content in the decomposition products are given in Table 1 together with the TG results. It is clear from the table that Cr(III) is completely oxidized into Cr(VI) when the mole ratio of KNO_3 to Cr_2O_3 is equal to and greater than three.



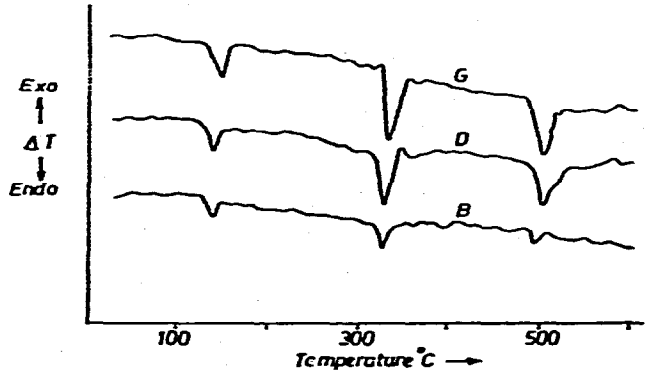


Fig. 1. TG plots of 1:2 (A), 1:1 (B), 2:1 (C), 3:1 (D), 4:1 (E), 5:1 (F), 6:1 (G), 8:1 (H) and 10:1 (I) molar ratios of KNO_3 and Cr_2O_3.

Fig 2. DTA plots of 1:1 (B), 3:1 (D) and 6:1 (G) molar ratios of KNO_3 and Cr_2O_3.

TABLE 1

THERMOGRAVIMETRIC AND ANALYTICAL DATA ON THE DECOMPOSITION OF POTASSIUM NITRATE AND CHROMIUM(III) OXIDE MIXTURES

Molar ratio KNO_3:Cr_2O_3	*Weight loss* (%)	*Analysis-found* (%) *Cr(VI)*	*Extent of Cr(III) oxidation* (%)
1:1	7.5	6.92	12.9
1:1	15.0	16.8	40.9
2:1	21.0	22.0	74.9
3:1	25.0	22.5	98.5
4:1	30.0	18.6	99.6
5:1	27.0	15.7	99.3
6:1	25.0	13.0	98.6
8:1	20.0	10.9	100.1
10:1	16.0	8.80	98.4

The decomposition products of the different molar ratios obtained around 600°C are subjected to infrared spectral analysis in order to identify the oxidized products. The spectra of the residues of mixtures 1:2, 1:1 and 2:1 are similar and had absorptions (cm^{-1}) at (407 w, 435 w, 555 m and 620 s) and (378 s, 460 w, 750 s, 790 sh, 885 s, 910 s, 920 s, 935 s and 1300 w). The first set of values corresponds[6] to that of Cr_2O_3 and the second set of values is due to $K_2Cr_2O_7$[7,8]. The residues of the mixtures 6:1, 8:1 and 10:1 showed absorptions (cm^{-1}) at 386 w, 400 w, 870 s, and 1240 w characteristic[7,8] of K_2CrO_4 and at 835 w, 1370 m and 1705 w due to the presence of undecomposed KNO_3[7]. The decomposition products of 3:1, 4:1 and 5:1 molar ratios showed infrared bands characteristic of both $K_2Cr_2O_7$ and K_2CrO_4. In addition, these residues had weak intensity bands around 1370 cm^{-1} characteristic[7] of free KNO_3. The infrared spectra of the residues of the mixtures of molar ratios greater than 3:1 exhibited very weak intensity bands at 835 and 1240 cm^{-1} due to KNO_2[7]. The hygroscopic nature of the residues and the alkalinity of their aqueous solutions confirm the formation of potassium oxide though KNO_2 is also hygroscopic.

The powder patterns of the decomposition products of 1:2, 1:1 and 2:1 molar ratios showed most intense lines (Å), 4.05, 3.89 and 2.10 characteristic[9] of Cr_2O_3 and 3.50 and 3.33 due to $K_2Cr_2O_7$[9]. The residues of 6:1 and higher molar ratios had intense d_{hkl} values (Å) 4.10 and 3.22 due to K_2CrO_4[9] and 3.75 and 3.00 characteristic[9] of KNO_3. The products of decomposition of 3:1, 4:1 and 5:1 molar ratios had d-spacings due to $K_2Cr_2O_7$, K_2CrO_4 and KNO_3.

From these results it is not possible to give the stoichiometric equation for the oxidation of Cr(III) without analysing the evolved nitrous oxides during the decomposition. However, from the plot of weight loss in mg per mmole of Cr_2O_3 against the mole ratio of KNO_3 to Cr_2O_3 (Fig. 3), it can be inferred that the amount of nitrous oxides liberated during the decomposition is constant when the mole ratio

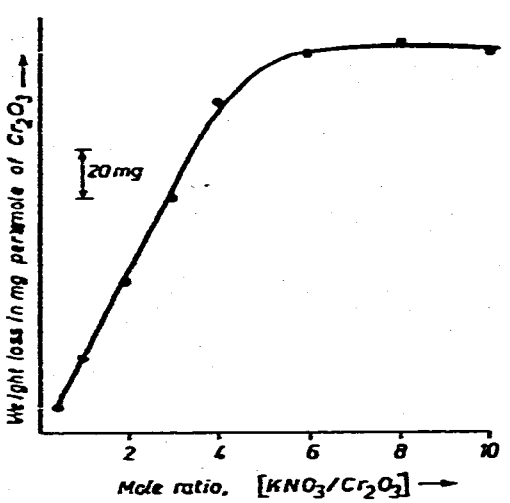


Fig. 3. Plot of mole ratio of KNO_3 to Cr_2O_3 versus weight loss in mg per mmole of Cr_2O_3.

is greater than six. That is, once the oxidation product of Cr(III) is K_2CrO_4, the excess KNO_3 present does not decompose below 600°C. In the case of mole ratios below six, though the oxidation is complete as observed in 3, 4 or 5, the product of oxidation is a mixture of $K_2Cr_2O_7$ and K_2CrO_4.

REFERENCES

1 S. Gordon and C. Campbell, *Anal. Chem.*, 27 (1955) 1102.
2 E. S. Freeman and D. Edelman, *Anal. Chem.*, 31 (1959) 624.
3 L. B. Berg, in R. C. Mackenzie (Ed.), *Differential Thermal Analysis*, Academic Press, London and New York, 1970, p. 356.
4 M. R. Udupa, *Thermochim. Acta*, 12 (1976) 165.
5 M. R. Udupa, *Thermochim. Acta*, 13 (1976) 349.
6 N. T. McDevitt and W. L. Baun, *Spectrochim. Acta*, 20 (1964) 799.
7 F. A. Miller and C. H. Wilkins, *Anal. Chem.*, 24 (1952) 1253.
8 F. A. Miller, G. L. Carlson, F. F. Bentley and W. H. Jones, *Spectrochim. Acta*, 16 (1960) 135.
9 *Index (Inorganic) to the Powder Diffraction File*, JCPDS, 1971.