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THERMAL DECOMPOSITION OF POTASSIUM CHLORATE IN PRESENCE OF CHROMIUM(III) OXIDE AND NICKEL(II) CHROMITE(III)

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ABSTRACT

A study of thermal behaviour of intimate mixtures of different molar ratios of potassium chlorate and chromium(III) oxide, and potassium chlorate and nickel(II) chromite(III) was made by employing thermogravimetry, differential thermal analysis, chemical analysis, infrared spectroscopy and X-ray powder diffraction analysis. Potassium chlorate in presence of Cr(III), starts decomposing around 200 °C which is much below the decomposition temperature of pure $KClO_3$. Each mole of Cr(III) takes up 8/3 moles of $KClO_3$ to become oxidized into potassium dichromate.

INTRODUCTION

The thermal behaviour of potassium chlorate has been studied by several investigators[1–4] and it is observed that $KClO_3$ melts around 350 °C and decomposes to give potassium chloride in the temperature range 400–580 °C. The catalytic effect of a series of metal oxides on the thermal behaviour of $KClO_3$ has been investigated by Freeman and Rudloff[4]. In the presence of metal oxides $KClO_3$ decomposes at lower temperatures and the catalytic influence of metal oxides on its decomposition is similar to that found on the decomposition of potassium perchlorate. Recently we have reported[5] the oxidation of Cr(III) into potassium dichromate during the thermal decomposition of intimate mixtures of Cr(III)–$KClO_4$ mixtures. In this work, the influence of chromium(III) oxide and nickel(II) chromite(III), $NiCr_2O_4$, on the thermal decomposition of $KClO_3$ in air, is studied in order to find out the extent of Cr(III) oxidation. The decomposition studies were made by making use of thermogravimetry and differential thermal analysis. The products of decomposition were characterized by chemical analyses, infrared spectral measurements and X-ray powder diffraction patterns.

EXPERIMENTAL

Materials

Commercially available potassium chlorate was recrystallized from hot water and was used. Chromium(III) oxide was obtained by heating reagent grade hydrated

chromium(III) nitrate at 500°C till the completion of decomposition. Nickel(II) chromite(III) was prepared by heating a 1:2 molar ratio of NiO, obtained by decomposing hydrated nickel nitrate at 500°C, and AnalaR CrO_3 to 800°C and keeping the sample at that temperature for 4 h. All other reagents used were of analytically pure grade.

Methods

Mixtures of $KClO_3$ and Cr_2O_3, and $KClO_3$ and $NiCr_2O_4$ were made in 1:2, 1:1, 2:1, 5:2, 8:3, 3:1, 4:1 and 8:1 molar ratios by taking the required amounts and grinding in an agate mortar for 15 to 20 min.

Thermogravimetric studies were made in air using a Stanton recording thermobalance at a linear heating rate of 6°C min^{-1}. About 250 mg samples were taken in platinum crucible containers. Differential thermal analyses were performed on a Netzch differential thermoanalyzer using inert alumina as reference material. About 50–100 mg samples were taken for each run and the heating rate of the furnace was maintained at 10°C min^{-1}. Constant temperature heating experiments were carried out on a muffle furnace whose temperature could be controlled with an accuracy of ±10°C using vitreosil crucible containers.

Infrared spectra were measured in the range 1400–300 cm^{-1} on a Beckman IR-12 spectrophotometer using both Nujol and KBr pellet techniques.

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

Analytical

Chromium(VI) in the reaction products was determined by the iodometric method; chloride was determined gravimetrically after separating the chromate by precipitating as barium chromate[6].

RESULTS AND DISCUSSION

The thermogravimetric and DTA plots of 1:1, 8:3 and 8:1 molar ratios of $KClO_3$ and Cr_2O_3 are given in Fig. 1. The TG and DTA curves of 1:2, 2:1 and 2:5 were similar to those of 1:1 whereas the curves of 3:1 and 4:1 were identical with those of 8:1. The thermograms suggest that the onset of decomposition occurs around 180°C for all the mixtures and the decomposition is complete by 380°C. In a separate experiment about 0.5–1 g samples of different mixtures were taken in vitreosil crucibles and heated to 400°C. The products of decomposition were subjected to chemical, infrared and X-ray diffraction analyses.

The residues of 8:3, 3:1, 4:1 and 8:1 $KClO_3$–Cr_2O_3 molar ratios are freely soluble in water, whereas the residues of 5:2, 2:1, 1:1 and 1:2 are partly soluble; the insoluble part is found to be unreacted Cr_2O_3. The aqueous solutions of all the residues contained both potassium dichromate and potassium chloride. The results of chemical analysis are given in Table 1.

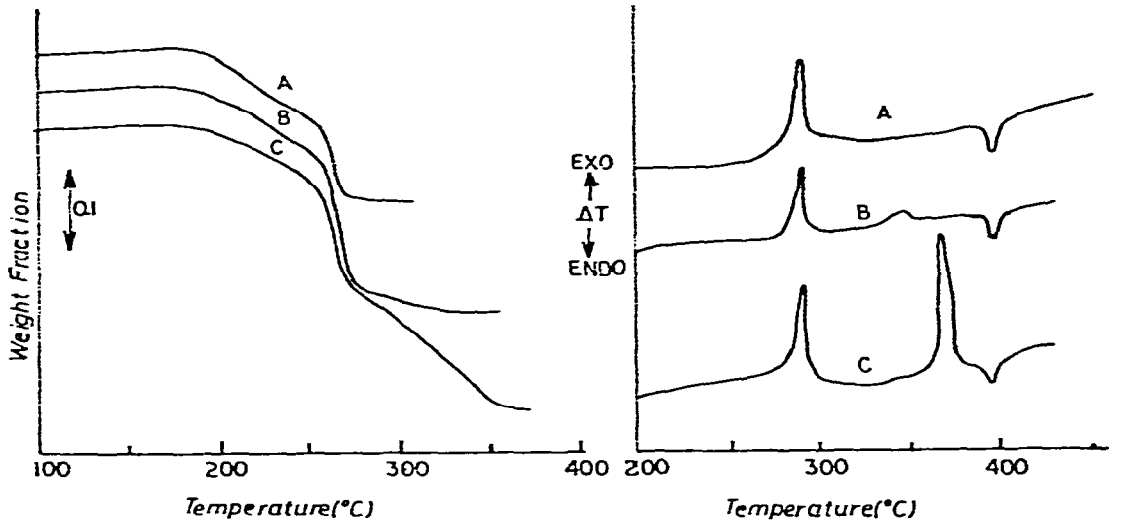

Fig. 1. TG and DTA plots of 1:1 (A), 8:3 (B) and 8:1 (C) molar ratios of $KClO_3$ and Cr_2O_3.

TABLE 1

ANALYTICAL DATA OF THE RESIDUES OF DECOMPOSITION OF POTASSIUM CHLORATE AND CHROMIUM(III) OXIDE MIXTURES

$KClO_3$:Cr_2O_3	*Cr(III) oxidized (%)*	*Extent of Cr(III) oxidation (%)*	*Chloride (%)*	
			Found	*Calc.*[a]
1:2	9.23	18.9	1.83	2.10
1:1	14.20	37.5	3.41	3.23
2:1	19.6	74.8	4.53	4.46
5:2	21.3	93.8	4.71	4.83
8:3	21.7	99.9	4.98	4.94
3:1	20.0	99.2	6.68	6.82
4:1	16.1	98.8	11.24	11.0
8:1	8.98	97.8	18.63	18.8

[a] As per reactions 1 and 2.

The infrared spectra of the products of decomposition of 8:3, 3:1, 4:1 and 8:1 were quite identical and had absorptions at (cm^{-1}) 1303 w, 950 s,b, 905 s, 890 s, 798 s, 760 s, 565 m, 450 w and 375 m. These values corresponded[7,8] to the absorption frequencies of pure $K_2Cr_2O_7$. On the other hand, the infrared spectra of the residues of other mixtures were similar to each other and had absorptions due to $K_2Cr_2O_7$ and additional frequencies (cm^{-1}) at 625 m, 558 m and 400 w which are characteristic[9] of Cr_2O_3 which confirmed the presence of free Cr_2O_3.

The X-ray powder patterns of the residues of 8:3, 3:1, 4:1 and 8:1 molar ratios had identical patterns with the following intense d_{hkl} values (Å), (3.65 m, 3.44 m, 2.95 s, 2.85 s, 2.60 w and 2.03 w) and (3.16 s, 2.22 m and 1.82 w). The first set of

values agreed[10] with the diffraction patterns of $K_2Cr_2O_7$ and the latter set matched with those of KCl. The powder photographs of the residues of the molar ratios less than 8:3 had identical patterns. The *d*-spacings corresponded to $K_2Cr_2O_7$ and KCl and in addition, there were extra lines (A) 3.63 m, 2.68 s, 2.47 s, and 1.68 s which agreed[10] with those of unreacted Cr_2O_3.

From the results of chemical analysis and infrared and X-ray diffraction data it is clear that, when the molar ratio of $KClO_3$ and Cr_2O_3 is equal to and greater than 8:3 Cr(III) in the mixture, it is completely oxidized into $K_2Cr_2O_7$ whereas in molar ratios less than 8:3, only a stoichiometric amount of Cr(III) is oxidized to $K_2Cr_2O_7$. The decomposition scheme is as follows:

$$xKClO_3 + Cr_2O_3 \rightarrow K_2Cr_2O_7 + (x-2)KCl + 2ClO_2\uparrow + (\tfrac{1}{2}x-4)O_2\uparrow \qquad x \geqslant \tfrac{8}{3} \qquad (1)$$

$$KClO_3 + yCr_2O_3 \rightarrow \tfrac{3}{8}K_2Cr_2O_7 + \tfrac{1}{4}KCl + (y-\tfrac{3}{8})Cr_2O_3 + \tfrac{3}{4}ClO_2\uparrow \qquad y \geqslant \tfrac{3}{8} \qquad (2)$$

Based on the reaction schemes 1 and 2 the expected weight-losses for different mixtures are calculated and the values are given in Table 2 together with the thermogravimetric results. The two values are in excellent agreement.

TABLE 2

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

$KClO_3$:Cr_2O_3		1:2	1:1	2:1	2:5	8:3	3:1	4:1	8:1
Weight loss (Wt. %)	Found	12.0	19.0	26.0	27.5	28.0	29.0	31.0	35.0
Weight loss (Wt. %)	Calc.	11.9	18.9	25.5	27.6	28.2	29.1	31.0	34.5

The DTA curves of $KClO_3$–Cr_2O_3 mixtures showed an exotherm around 280 °C due to the oxidation of Cr(III) leading to the formation of $K_2Cr_2O_7$ and an endotherm at 400 °C which is attributed to the melting of $K_2Cr_2O_7$. A small exotherm around 350 °C observed for 8:3 and higher mixtures is assigned to the complete oxidation of Cr(III). A prominent exotherm at 380 °C observed for mixtures greater than 8:3 is due to the decomposition of excess $KClO_3$.

In Fig. 2 are given the thermogravimetric and DTA curves of 1:1, 8:3, and 8:1 molar ratios of $KClO_3$ and $NiCr_2O_4$. The plots of TG and DTA for 3:1 and 4:1 molar ratios are similar to those of 8:1 whereas those of lower mixtures are similar to the plots of 1:1 molar ratio. The TG curves suggest that the mixtures started decomposing around 200 °C, a slightly higher temperature than that observed for $KClO_3$–Cr_2O_3 mixtures but much lower than that of pure $KClO_3$. The decomposition was complete by 380 °C. As in the case of $KClO_3$–Cr_2O_3 system, different molar ratios

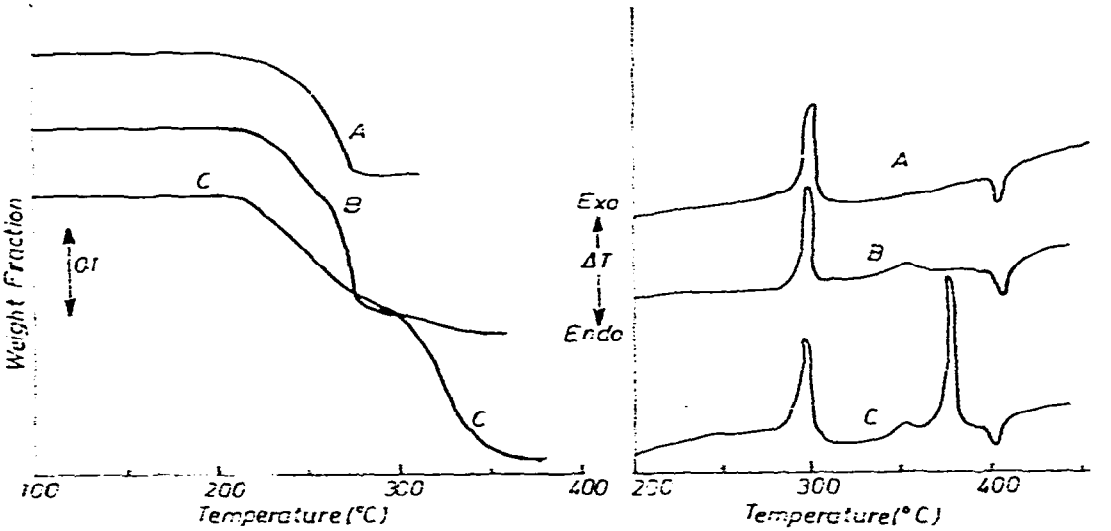

Fig. 2. TG and DTA plots of 1:1 (A), 8:3 (B) and 8:1 (C) molar ratios of $KClO_3$ and $NiCr_2O_4$.

of $KClO_3$ and $NiCr_2O_4$ are heated to 400 °C and the products of decomposition are analysed. The residues of the mixture are not completely soluble in all the cases. However, the insoluble part in the mixtures equal to and greater than 8:3 is soluble in dil. acids and is found to be nickel oxide. On the other hand, the insoluble part in the residues of the molar ratios less than 8:3 is partly soluble in dil. acids; the soluble part is found to be nickel oxide and the acid insoluble part is found to be unreacted $NiCr_2O_4$. The analytical results of the residues of different mixtures are given in Table 3.

The infrared spectra of the residues of mixtures 8:3, 3:1, 4:1 and 8:1 are all identical and had absorptions characteristic of $K_2Cr_2O_7$ with additional frequencies

TABLE 3

ANALYTICAL DATA ON RESIDUES OF DECOMPOSITION OF POTASSIUM CHLORATE AND NICKEL(II) CHROMITE(III)

$KClO_3$:$NiCr_2O_4$	*Cr(III) oxidized* (%)	*Extent of Cr(III) oxidation* (%)	*Chloride* (%)	
			Found	*Calc.*[a]
1:2	6.87	19.0	1.64	1.56
1:1	11.2	37.7	2.25	2.57
2:1	16.7	75.7	3.88	3.79
5:2	18.4	94.3	4.33	4.18
8:3	18.9	100.1	4.43	4.30
3:1	17.4	99.4	6.21	6.00
4:1	14.3	98.6	9.87	9.95
8:1	8.43	97.8	18.0	17.7

[a] As per reactions 3 and 4.

(cm^{-1}) at 648 w, 465 s,b, and 478 w which are due to NiO[9]. The spectra of the decomposition products of 1:2, 1:1, 2:1 and 5:2 were quite similar and had major frequencies due to $K_2Cr_2O_7$ and NiO. In addition, the spectra had additional absorptions (cm^{-1}) at 628 s, 600 s, 510 m, 413 w, 338 w and 300 w which are due to unreacted $NiCr_2O_4$.

The X-ray powder photographs of 8:3, 3:1, 4:1 and 8:1 molar ratios had identical patterns. The *d*-spacings corresponded to $K_2Cr_2O_7$ and KCl with additional lines (Å) at 2.40 s, 2.11 s, 1.49 w due to NiO[10]. The powder patterns of the residues of molar ratios lower than 8:3 had d_{hkl} values characteristic of $K_2Cr_2O_7$, KCl, NiO and unreacted $NiCr_2O_4$.

Based on these results, the decomposition scheme of $KClO_3$ and $NiCr_2O_4$ mixtures can be given similar to that of $KClO_3$ and Cr_2O_3 mixtures as:

$$xKClO_3 + NiCr_2O_4 \rightarrow K_2Cr_2O_7 + (x-2)KCl + NiO + 2ClO_2\uparrow + (\tfrac{3}{2}x-4)O_2\uparrow, \quad x \geqslant \tfrac{8}{3} \tag{3}$$

$$KClO_3 + yNiCr_2O_4 \rightarrow \tfrac{3}{8}K_2Cr_2O_7 + \tfrac{3}{8}NiO + (y-\tfrac{3}{8})NiCr_2O_4 + \tfrac{3}{4}ClO_2\uparrow \quad y \geqslant \tfrac{3}{8} \tag{4}$$

The TG results of the decomposition of different mixtures together with the calculated values on the basis of reactions 3 and 4 are given in Table 4. The two results agree with each other.

TABLE 4

THERMOGRAVIMETRIC DATA ON THE DECOMPOSITION OF DIFFERENT MOLAR RATIOS OF POTASSIUM CHLORATE AND NICKEL(II) CHROMITE(III)

$KClO_3$:$NiCr_2O_4$		1:2	1:1	2:1	5:2	8:3	3:1	4:1	8:1
Weight loss (Wt. %)	Found	9.0	14.5	21.5	24.0	24.5	25.0	28.0	33.0
Weight loss (Wt. %)	Calc.	8.69	14.2	21.0	23.9	24.1	25.0	27.4	32.2

The exothermic DTA peak observed around 280 °C is ascribed to the oxidation of Cr(III) into Cr(VI), and an endotherm around 400 °C is due to the melting of $K_2Cr_2O_7$. The exotherm observed at 380 °C for the molar ratios greater than 8:3 is attributed to the decomposition of excess $KClO_3$. A small exotherm around 350 °C is due to the complete oxidation of Cr(III) as observed in the case of the $KClO_3$–Cr_2O_3 mixtures.

The decomposition of $KClO_3$ in excess to that required for the complete oxidation of Cr(III) in the mixture with molar ratios greater than 8:3 takes place immediately after most of Cr(III) is oxidized, and is complete at 380 °C. It is reported[4] that NiO has catalytic influence on the thermal decomposition of $KClO_3$. In order to find out the influence of $K_2Cr_2O_7$ on the decomposition and to compare the effects

of NiO and $K_2Cr_2O_7$, thermal decomposition studies of intimate mixtures of 2:1 molar ratios of $KClO_3$ and $K_2Cr_2O_7$, and $KClO_3$ and NiO were made. The TG and DTA plots of the decomposition are given in Fig. 3. The $KClO_3$–$K_2Cr_2O_7$ mixture started to decompose around 280°C and was complete at 380°C. The weight-loss

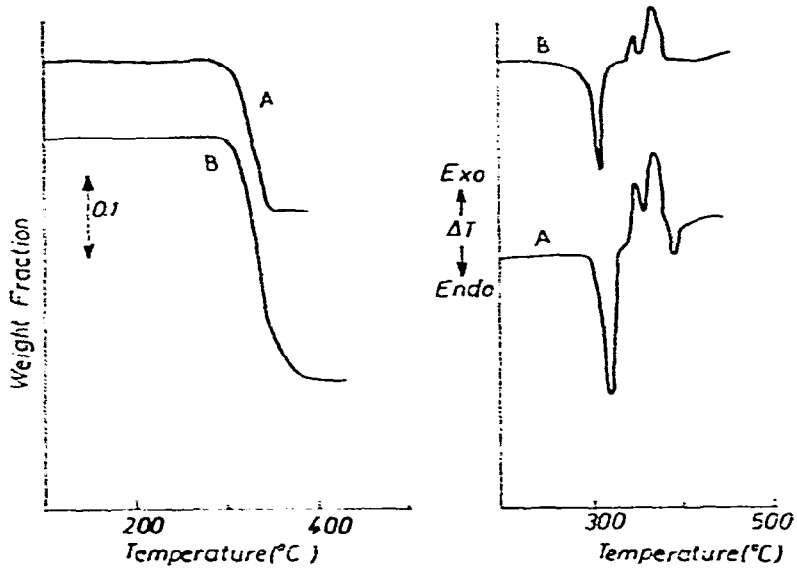

Fig. 3. TG and DTA plots of 2:1 molar ratios of $KClO_3$ and $K_2Cr_2O_7$ (A) and $KClO_3$ and NiO.

observed at 380°C was 18.0% whereas that calculated for the complete decomposition of $KClO_3$ was 17.8%. The product was analyzed, and was confirmed to be $K_2Cr_2O_7$ and KCl. On the other hand the onset of decomposition for the $KClO_3$–NiO mixture was at 300°C and the decomposition was complete by 400°C. The weight-loss observed after the completion of the decomposition was 30.0% and that calculated for the formation of KCl was 30.0%. The DTA plots of the mixtures gave an endothermic peak around 325°C due to the fusion of $KClO_3$ followed by two exothermic peaks at 350 and 370°C which are the characteristic of $KClO_3$ decomposition[4]. The endotherm around 400°C observed in the $KClO_3$–$K_2Cr_2O_7$ mixture is due to the contact with $K_2Cr_2O_7$. The results indicate that $KClO_3$ decomposition is more influenced in presence of $K_2Cr_2O_7$ than NiO, though both have the catalytic effect on its decomposition.

It is interesting to note that though there is sufficient oxygen in $KClO_3$ in the molar ratios, 5:2 and 2:1, Cr(III) in these mixtures is incompletely oxidized. This is probably, chlorine dioxide, one of the decomposition products of $KClO_3$ escapes as such, without oxidizing Cr(III).

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