Thermochimica Acta, 12 (1975) 165–172

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

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(Received 16 December 1974)

ABSTRACT

A study of the thermal decomposition of intimate mixtures of different molar ratios of potassium perchlorate and chromium(III) oxide, and potassium perchlorate and nickel(II) chromite(III) was conducted employing thermogravimetry, differential thermal analysis, chemical analysis, infrared spectroscopy and X-ray diffraction analysis. Upon heating to 400°C Cr(III), in 2:1 molar ratios, is oxidized to potassium dichromate. Only a stoichiometric amount of Cr(III) was oxidized from molar ratios less than 2:1, leaving behind excess Cr_2O_3 and $NiCr_2O_4$ whereas from molar ratios greater than 2:1, Cr(III) was completely oxidized and the excess $KClO_4$ started decomposing around 410°C which is much below the decomposition temperature of pure $KClO_4$.

INTRODUCTION

Several investigators[1–3] have studied the thermal decomposition of potassium perchlorate and found that it started to decompose at 590°C after a phase transformation from orthorhombic to cubic at 300°C. The influence of metal oxides on the thermal decomposition of potassium perchlorate has been studied by Markowitz and Boryta[4] and Freeman and Anderson[5]. It is reported[6] that the metal oxides act as catalysts and the decomposition temperature of potassium perchlorate in the presence of these oxides is considerably lower than that of pure potassium perchlorate. The catalytic effect has been attributed to the abstraction of atomic oxygen from the perchlorate moiety and there is no report on any compound formation due to the interaction. Recently, we have reported[7] the formation of thallium(I) dichromate during the thermal decomposition of thallium(I) perchlorate in the presence of chromium(III) oxide. In this work, the influence of chromium(III) oxide and nickel(II) chromite(III), ($NiCr_2O_4$), on the thermal decomposition of potassium perchlorate in air and the characteristics of the products is studied. Thermogravimetry, differential thermal analysis, chemical analysis, X-ray powder diffraction analysis and infrared spectral data have been employed to obtain the desired information.

EXPERIMENTAL

Materials

Potassium perchlorate used was from BDH (London). Chromium(III) oxide was obtained by heating reagent grade $Cr(NO_3)_3 \cdot 9H_2O$ at 400°C until the decomposition was complete. Nickel(II) chromite(III) was prepared by heating an intimate mixture of NiO, obtained by the decomposition of $Ni(NO_3)_2 \cdot 6H_2O$ at 400°C, and AnalaR CrO_3 in 1:2 molar ratio to 800°C and keeping the sample at that temperature for 4 h. The product obtained was insoluble both in acids and alkalis and gave d_{hkl} values (Å), 4.77 w, 2.92 m, 2.51 s, 2.09 m, 1.60 m and 1.47 s, which agreed very well with the literature value[8] of $NiCr_2O_4$. All other reagents used were of analytically pure grade.

Methods

Mixtures of $KClO_4$ and Cr_2O_3, and $KClO_4$ and $NiCr_2O_4$ were prepared in 1:2, 1:1, 2:1, 4:1 and 8:1 molar ratios by taking the required amounts and grinding in an agate mortar for 20 to 30 min.

Thermogravimetric studies were made in air using a Stanton recording thermobalance at a heating rate of 6°C min^{-1}. About 250 mg samples were taken in platinum crucible containers. Differential thermal analyses were done on a Netzsch differential thermal analyser using inert alumina as reference material. About 50–70 mg of the samples were taken for each run and the heating rate of the furnace was kept 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 ±5°C using vitreosil crucible containers. Furnace temperatures were selected on the basis of thermogram results.

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

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

Analytical

Chromium(VI) in the reaction products was determined by the iodometric method; nickel(II) in free NiO was determined gravimetrically by dissolving in dil. acid and employing dimethylglyoxime reagent. Chloride was determined gravimetrically after separating the chromate by precipitating as barium chromate[9].

RESULTS AND DISCUSSION

The thermogravimetric results of five different molar ratios of $KClO_4$ and Cr_2O_3 are given in Table 1. The TG and DTA curves of 1:1, 2:1 and 8:1 mixtures are reproduced in Fig. 1. Thermograms and DTA plots of 1:2 and 4:1 mixtures were similar to those of 1:1 and 8:1, respectively. The X-ray diffraction patterns of the

TABLE 1

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

$KClO_4$:Cr_2O_3	*Weight loss (wt. %)*			
	Plateau I		*Plateau II*	
	Found	*Calc.*	*Found*	*Calc.*[a]
1:2	15.0	15.25[b]	—	—
1:1	23.0	23.20[c]	—	—
2:1	31.5	31.44[c]	—	—
4:1	19.0	19.11[c]	37.0	37.24
8:1	10.5	10.70[c]	41.0	41.19

[a] As per reaction (3). [b] As per reaction (1). [c] As per reaction (2).

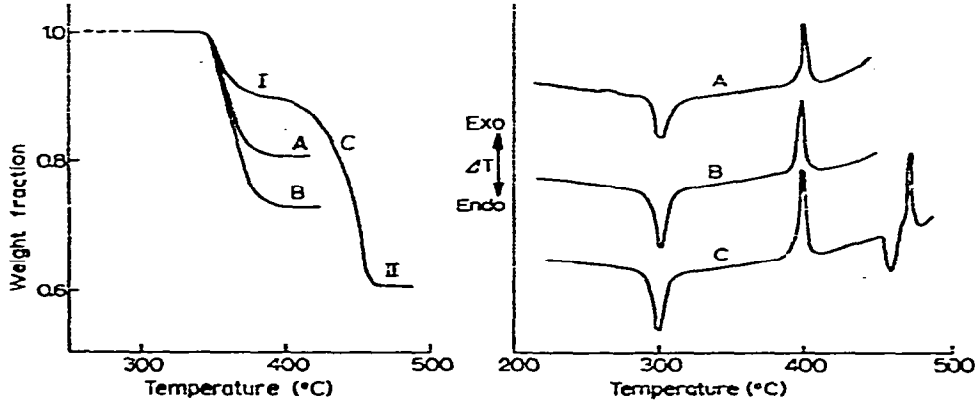

Fig. 1. TG and DTA plots of 1:1 (A), 2:1 (B) and 8:1 (C) molar ratios of $KClO_4$ and Cr_2O_3.

product obtained for the 2:1 molar ratio gave the following d_{hkl} values (Å): 3.66 m, 3.44 m, 3.28 s, 3.01 s, 2.85 s, 2.60 w and 2.03 w. These values are in excellent agreement[8] with those found for pure $K_2Cr_2O_7$. No extraneous lines were observed. The X-ray powder photographs of 1:1 and 1:2 mixtures gave the *d*-spacings corresponding to $K_2Cr_2O_7$ and extra lines (Å) at 3.63 m, 2.68 s, 2.48 s and 1.66 s which agreed with excess Cr_2O_3. On the other hand, the X-ray diffraction patterns of the residues of 4:1 and 8:1 molar ratios heated at 390°C (corresponding to plateau I in Fig. 1) till the constancy in weight was observed, gave all the major lines for $K_2Cr_2O_7$ and additional lines (Å) at 3.50 s, 3.15 s and 2.90 m which are characteristic of room temperature, orthorhombic form of $KClO_4$.

The infrared spectrum of the residue of 2:1 molar mixture gave the following frequencies (cm^{-1}) 1305 w, 950 s, b, 905 s, 890 s, 795 s, 760 s, 568 m, 450 w and 378 m. These values agreed[10,11] very well with the reported infrared spectra of pure

$K_2Cr_2O_7$. The spectra of the products of decomposition of 1:2 and 1:1 mixtures had all the bands for $K_2Cr_2O_7$ and additional absorptions (cm^{-1}) at 625 m, 560 m and 400 w which correspond[12] to those of Cr_2O_3. The infrared spectra of the products of decomposition of 4:1 and 8:1 mixtures corresponding to plateau I of Fig. 1, had all the absorptions for $K_2Cr_2O_7$ and additional frequencies due to perchlorate[10] of $KClO_4$ at (cm^{-1}) 1140 sh, 1075 s, 940 m and 630 s. Thus the infrared results agreed with those of X-ray diffraction studies.

Further data to support the formation of $K_2Cr_2O_7$ around 390°C are the results of chemical analyses. Different molar ratios of $KClO_4$ and Cr_2O_3 were heated at 390°C for 30 min and the products were analysed for Cr(VI) content. The extent of Cr(III) oxidation was computed and the results are given in Table 2. No chloride

TABLE 2

DATA ON HEATING MIXTURES OF POTASSIUM PERCHLORATE AND CHROMIUM(III) OXIDE MIXTURES

$KClO_4$:Cr_2O_3	*At 390°C*		*At 470°C*	
	Cr(III) oxidized (%)	*Extent of Cr(III) oxidation (%)*	*Chloride (%)*	
			Found	*Calc.*[a]
1:2	11.86	25.3	—	—
1:1	18.00	50.3	—	—
2:1	24.01	99.1	—	—
4:1	14.48	98.3	10.34	10.04
8:1	8.05	97.5	17.26	16.88

[a] As per reaction (3).

was found to be present in these residues. The concurrence of these results with the X-ray and infrared data is quite good. Based on these results the decomposition scheme of $KClO_4$ and Cr_2O_3 mixtures is as follows:

$$2KClO_4 + xCr_2O_3 \rightarrow K_2Cr_2O_7 + (x-1)\,Cr_2O_3 + Cl_2\uparrow + 2O_2\uparrow \quad x \geq 2 \qquad (1)$$

$$yKClO_4 + Cr_2O_3 \rightarrow K_2Cr_2O_7 + (y-2)\,KClO_4 + Cl_2\uparrow + 2O_2\uparrow \quad y \geq 2 \qquad (2)$$

The products of decomposition of 4:1 and 8:1 mixtures at 475°C (plateau II in Fig. 1), on X-ray analysis, gave *d*-spacings corresponding to $K_2Cr_2O_7$ with additional lines (Å) at 3.16 s, 2.22 m and 1.82 w, which are characteristic[8] of KCl. The infrared spectra were similar to those of pure $K_2Cr_2O_7$. On chemical analysis (Table 2), it was confirmed that the residues are the mixtures of $K_2Cr_2O_7$ and KCl. The second stage decomposition for the mixtures with a molar ratio higher than 2:1 involves the decomposition of unreacted $KClO_4$. The overall reaction is:

$$yKClO_4 + Cr_2O_3 \rightarrow K_2Cr_2O_7 + (y-2)\,KCl + Cl_2\uparrow + 2(y-1)O_2\uparrow \quad y \geq 2 \qquad (3)$$

The DTA runs of the mixtures showed an endotherm at 300°C attributed[1] to the phase transition of $KClO_4$ and an exotherm at 400°C due to the formation of $K_2Cr_2O_7$. Although pure $K_2Cr_2O_7$ is found to show an endotherm at 398°C due to its melting, the exothermicity of the formation of $K_2Cr_2O_7$ is greater, and hence only an exotherm is observed. For 4:1 and 8:1 mixtures, additional DTA peaks, an endotherm at 460°C immediately followed by an exotherm at 470°C, are observed which are ascribed[6] to the decomposition of $KClO_4$.

TABLE 3

TG DATA ON THE THERMAL DECOMPOSITION OF POTASSIUM PERCHLORATE AND NICKEL(II) CHROMIUM(III) OXIDE SPINEL

$KClO_4$:$NiCr_2O_4$	*Weight loss (wt. %)*			
	Plateau I		*Plateau II*	
	Found	*Calc.*	*Found*	*Calc.*[a]
1:2	11.50	11.40[b]	—	—
1:1	18.50	18.47[b]	—	—
2:1	27.0	26.78[c]	—	—
4:1	17.0	17.28[c]	34.0	33.67
8:1	10.0	10.10[c]	39.0	38.87

[a] As per reaction (6). [b] As per reaction (4). [c] As per reaction (5).

The influence of $NiCr_2O_4$ on the thermal decomposition of $KClO_4$ was similar to that of Cr_2O_3. The thermogravimetric results of the decomposition of the different mixtures of $KClO_4$ and $NiCr_2O_4$ are given in Table 3 and TG and DTA plots of 1:1, 2:1 and 8:1 mixtures are given in Fig. 2. The decomposition products obtained by heating the mixtures at 390°C were examined by X-ray, infrared and chemical analyses. The residue of 2:1 mixture gave X-ray patterns, characteristic of $K_2Cr_2O_7$

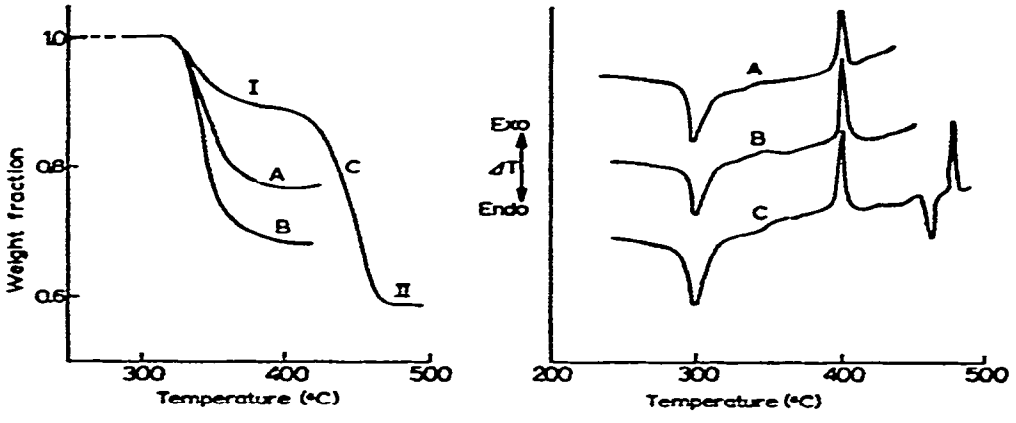

Fig. 2. TG and DTA plots of 1:1 (A), 2:1 (B) and 8:1 (C) molar ratios of $KClO_4$ and $NiCr_2O_4$.

with additional lines (Å) at 2.41 s, 2.10 s and 1.50 m due to NiO[8]. The powder patterns of the residues of 1:2 and 1:1 molar ratios were similar and had *d*-spacings corresponding to $K_2Cr_2O_7$, NiO and unreacted $NiCr_2O_4$. Whereas the residues at 390°C (plateau I in Fig. 2) of 4:1 and 8:1 mixtures had the X-ray patterns characteristic of $K_2Cr_2O_7$, NiO and $KClO_4$, the products of decomposition at 470°C (plateau II in Fig. 2) had *d*-spacings of $K_2Cr_2O_7$, NiO and KCl.

The infrared spectrum of the residue of the 2:1 mixture had absorptions due to $K_2Cr_2O_7$ and additional frequencies (cm^{-1}) at 650 w, 465 s, b and 480 w which are characteristic of NiO[12]. The spectra of the decomposition products of 1:2 and 1:1 mixtures 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 630 s, 600 s, 510 m, 415 w, 340 w and 300 w which are due to unreacted $NiCr_2O_4$. Whereas the spectra of the decomposition products of 4:1 and 8:1 mixtures at 390°C had absorptions due to $K_2Cr_2O_7$, NiO and $KClO_4$, the spectra of the residues of these mixtures at 470°C gave absorptions for $K_2Cr_2O_7$ and NiO.

Chemical analyses of the decomposition products of different mixtures are carried out and the results are given in Table 4. The decomposition product of the 2:1 mixture corresponded to the equimolar mixture of $K_2Cr_2O_7$ and NiO. The higher

TABLE 4

DATA ON HEATING MIXTURES OF POTASSIUM PERCHLORATE AND NICKEL(II) CHROMIUM(III) OXIDE SPINEL

$KClO_4$:$NiCr_2O_4$	*At 390°C*		*At 470°C*	
	Cr(III) oxidized (%)	*Extent of Cr(III) oxidation (%)*	*Chloride (%)*	
			Found	*Calc.*[a]
1:2	8.89	25.3	—	—
1:1	14.52	51.0	—	—
2:1	20.48	99.2	—	—
4:1	13.11	98.3	8.89	9.08
8:1	7.62	98.7	15.81	15.93

[a]As per reaction (6).

molar ratios at 390°C contained unreacted $KClO_4$ whereas the lower ratios contained unreacted $NiCr_2O_4$. The analysis of the residues at 470°C of the mixtures with a molar ratio greater than 2:1 gave $K_2Cr_2O_7$, NiO and KCl. Based on these results, the decomposition scheme of $KClO_4$ and $NiCr_2O_4$ mixtures can be given similar to that of $KClO_4$ and Cr_2O_3 mixtures as:

$$2KClO_4 + xNiCr_2O_4 \rightarrow K_2Cr_2O_7 + (x-1)\,NiCr_2O_4 + NiO + Cl_2\uparrow + 2O_2\uparrow \qquad x \geqslant 2 \qquad (4)$$

$$yKClO_4 + NiCr_2O_4 \rightarrow K_2Cr_2O_7 + (y-2)\,KClO_4 + NiO + Cl_2\uparrow + 2O_2\uparrow \qquad y \geqslant 2 \qquad (5)$$

$$yKClO_4 + NiCr_2O_4 \rightarrow K_2Cr_2O_7 + (y-2)\,KCl + NiO + Cl_2\uparrow + 2(y-1)O_2\uparrow \quad y \geqslant 2 \qquad (6)$$

The DTA peaks observed at 300 °C due to phase transformation of $KClO_4$ and at 400 °C due to the formation of $K_2Cr_2O_7$ are similar to those found in $KClO_4$ and Cr_2O_3 mixtures. The peaks observed around 470 °C are attributed[6] to the decomposition of $KClO_4$.

The decomposition of $KClO_4$ in excess to that required for the complete oxidation of Cr(III) in the mixture with a molar ratio greater than 2:1, started at 410 °C and was complete at 470 °C. This temperature range is much lower than that of pure $KClO_4$. It is reported[6] that NiO has a catalytic effect on the thermal decomposition of $KClO_4$. In order to find out the influene 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 $KClO_4$ and $K_2Cr_2O_7$, and $KClO_4$ and NiO were made. The TG and DTA plots of the decomposition are given in Fig. 3. The $KClO_4$–$K_2Cr_2O_7$ mixture started to decompose around 380 °C and was complete by 470 °C.

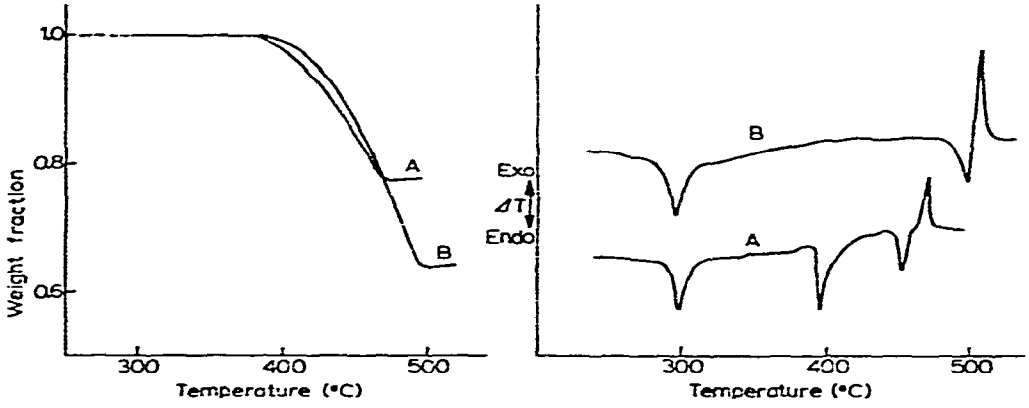

Fig. 3. TG and TDA plots of 2:1 molar ratios of $KClO_4$ and $K_2Cr_2O_7$ (A) and $KClO_4$ and NiO (B).

The weight loss observed at 470 °C was 22.5% whereas that expected for the complete decomposition of $KClO_4$ was 22.4%. Chemical analysis of the product confirmed it to be a mixture of $K_2Cr_2O_7$ and KCl. The $KClO_4$–NiO mixture on the other hand, started to decompose around 400 °C and was complete at 500 °C. The weight loss observed for the decomposition was 36.5% and that expected for the formation of KCl was 36.4%. The DTA plots of the mixtures gave an endothermic peak at 300 °C due to phase transformation of $KClO_4$. An endotherm at 400° C for the $KClO_4$–$K_2Cr_2O_7$ mixture was due to the melting of $K_2Cr_2O_7$. At higher temperatures, an endotherm followed by an exotherm is attributed[6] to the decomposition of $KClO_4$. The results indicate that the decomposition of $KClO_4$ is more influenced by the presence of $K_2Cr_2O_7$ than NiO, though both catalyze its decomposition.

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