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## Note

# Thermal behaviour of potassium perchlorate and potassium chlorate in presence of chromium(VI) oxide

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The catalytic influence of metal oxides on the decomposition of potassium perchlorate and potassium chlorate has been reviewed by Rudloff and Freeman[1] and it has been observed that the decomposition temperatures of potassium perchlorate and potassium chlorate in the presence of several of these oxides are considerably lower than those of the pure salts. It is suggested that the chemical reactions are involved in the decomposition of potassium chlorate in the presence of chromium(VI) oxide rather than true catalysis. Studies on the thermal decomposition of potassium perchlorate[2] and potassium chlorate[3] in the presence of $Cr_2O_3$ have revealed that chromium(III) oxide not only lowers the decomposition temperatures of pure potassium salts but chemically interacts to form potassium dichromate; each mole of $Cr_2O_3$ consumes 2 moles of $KClO_4$ and 8/3 moles of $KClO_3$. The present work deals with the detailed studies made of the effect of $CrO_3$ on the thermal decomposition of $KClO_4$ and $KClO_3$ employing TG and DTA techniques. The decomposition products were examined by chemical analysis, infrared spectral measurements and X-ray powder patterns.

## EXPERIMENTAL

### *Materials*

Potassium perchlorate used was from BDH (London). Commercially available potassium chlorate was recrystallized and used. All other chemicals employed were pure reagent grade.

### *Methods*

Mixtures of $KClO_4$ and $CrO_3$, and $KClO_3$ and $CrO_3$ were prepared in 1:2, 1:1, 2:1 and 4:1 molar ratios by taking the required amounts and grinding in an agate mortar for 5–10 min.

The thermogravimetric analyses were made in air using Stanton recording thermobalance at a linear heating rate of 6°C $min^{-1}$. About 200 mg samples were taken in a platinum crucible container for each run. Differential thermal analyses were made in air employing Netzsch differential thermoanalyzer at a heating rate of

10°C $min^{-1}$ using standard alumina as reference material. About 70–100 mg samples were used for each experiment in platinum crucible container.

The infrared spectra were recorded in Nujol on Beckman IR 12 spectrophotometer. The X-ray powder patterns were taken with a Debye-Scherrer 114.6 mm diam. camera using Cu$K_\alpha$ radiation.

*Analytical*[4]

Chromium(VI) was determined iodometrically. Chloride was determined gravimetrically after separating the chromate by precipitating as barium chromate.

## RESULTS AND DISCUSSION

In Figs. 1 and 2 are given TG and DTA plots of 1:2, 1:1 and 2:1 molar ratios of $KClO_4$ and $CrO_3$, and $KClO_3$ and $CrO_3$, respectively. As the plots of 4:1 mixtures are similar to the corresponding 2:1 molar ratios, they are not reproduced. For the sake of comparison, the TG and DTA curves of $CrO_3$ are plotted in Fig. 1A. The observed nature of $CrO_3$ decomposition is similar to that of an earlier report[5]. It melts around 220°C, indicated by an endotherm and starts decomposing at 300°C. A broad exotherm around 350°C is attributed to the expulsion of oxygen and an endotherm at 480°C is due to the formation of $Cr_2O_3$. The decomposition begins at 240°C for all the mixtures of $KClO_4$ and $CrO_3$, and at 200°C for those of $KClO_3$ and $CrO_3$, which are much lower than the decomposition temperatures of pure $KClO_4$[2] and $KClO_3$[3]. For 1:1 molar ratios the decomposition was complete at 350°C for the $KClO_4$–$CrO_3$ system and at 250°C for the $KClO_3$–$CrO_3$ system. The decomposition was complete at 480°C for 1:2 molar ratios of the two systems and at 450 and 350°C for 2:1 and 4:1 molar ratios of $KClO_4$–$CrO_3$ and $KClO_3$–$CrO_3$ mixtures, respectively. The residues of decomposition of all mixtures are examined by chemical analyses and infrared and X-ray diffraction studies.

The products of decomposition of 1:1, 2:1 and 4:1 molar ratios are soluble freely in water and contained $K_2Cr_2O_7$ and KCl. The residues of the 1:2 mixtures are partly soluble and contained $K_2Cr_2O_7$ and $Cr_2O_3$. The analytical values are given in Tables 1 and 2.

The infrared spectra of the decomposition products of 1:1, 2:1 and 4:1 molar ratios of the two systems are identical and had absorptions at ($cm^{-1}$) 1303w, 950s,b, 903s, 892s, 800s, 760s, 562m, 450w, 372m which corresponded[6,7] to the absorption frequencies of pure $K_2Cr_2O_7$. On the other hand the infrared spectra of the residues of 1:2 mixtures had absorptions due to $K_2Cr_2O_7$ and additional frequencies at ($cm^{-1}$) 625s, 555m and 400w which are characteristic[8] of $Cr_2O_3$ indicating the presence of free $Cr_2O_3$.

The X-ray powder patterns of the residues of 1:1 molar ratios of the two systems had the following intense $d_{hkl}$ values (Å): 3.65m, 3.44m, 2.95s, 2.85s, 2.60w and 2.03w. These values are due to the diffraction patterns of $K_2Cr_2O_7$[9]. The decomposition products of higher molar ratios had *d*-spacings due to $K_2Cr_2O_7$ with

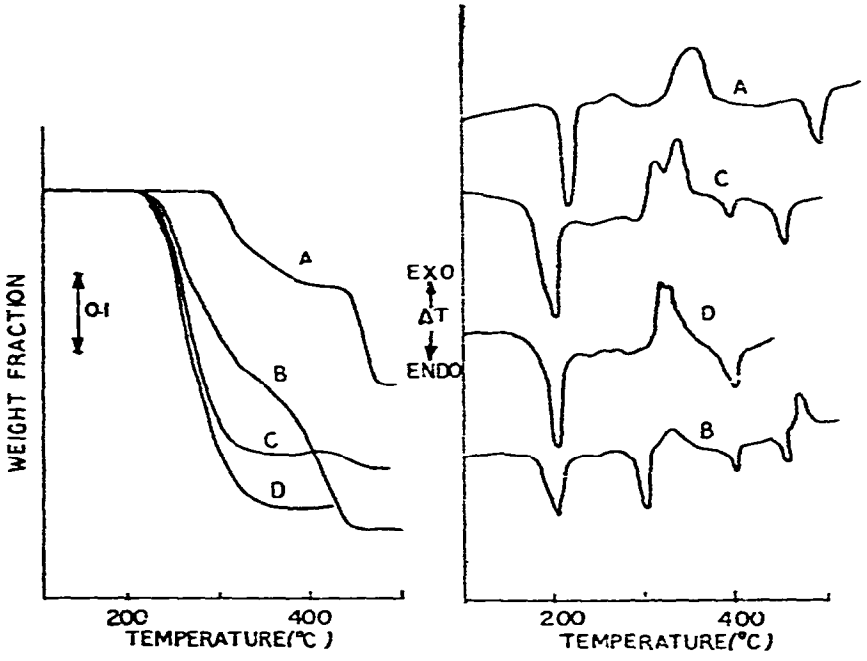


Fig. 1. TG and DTA plots of $CrO_3$ (A) and 1:2 (B), 1:1 (D) and 2:1 (C) molar ratios of $KClO_4$ and $CrO_3$.

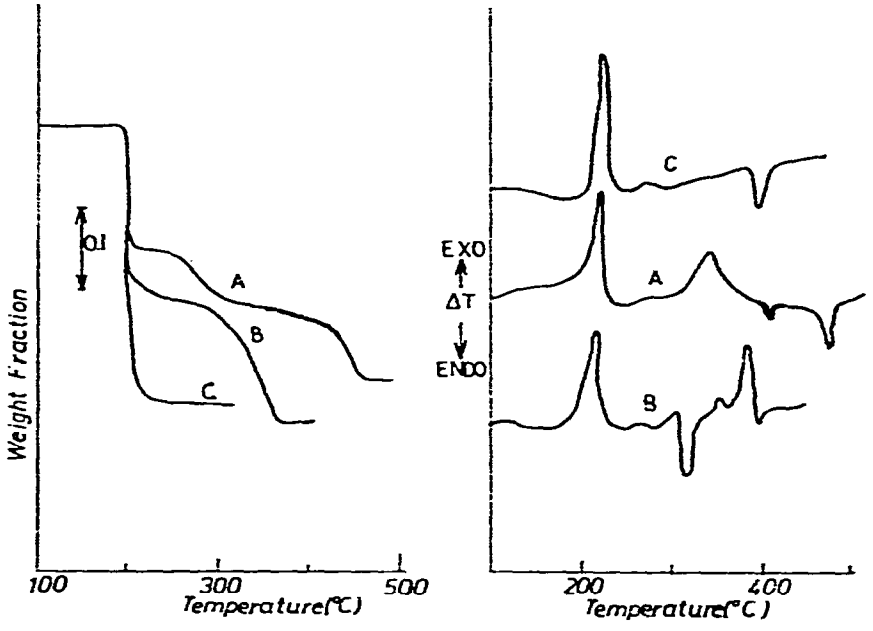


Fig. 2. TG and DTA plots of 1:2 (A), 1:1 (C) and 2:1 (B) molar ratios of $KClO_3$ and $CrO_3$.

TABLE 1

TG AND ANALYTICAL DATA ON $KClO_4$ AND $CrO_3$ MIXTURES

| *Molar ratio* $KClO_4$:$CrO_3$ | *Weight loss (%)* | | *Found* | | *Calc.* | |
|---|---|---|---|---|---|---|
| | *Found* | *Calc.* | *Cr (VI)* | *Cl* | *Cr (VI)* | *Cl* |
| 1:2 | 34.5 | 34.0 | 15.7 | — | 15.4 | — |
| 1:1 | 38.5 | 38.4 | 22.1 | — | 21.8 | — |
| 2:1 | 41.5 | 41.2 | 13.4 | 9.12 | 13.8 | 9.40 |
| 4:1 | 43.5 | 43.3 | 8.24 | 16.2 | 7.95 | 16.3 |

TABLE 2

TG AND ANALYTICAL DATA ON $KClO_3$ AND $CrO_3$ MIXTURES

| *Molar ratio* $KClO_3$:$CrO_3$ | *Weight loss (%)* | | *Found* | | *Calc.* | |
|---|---|---|---|---|---|---|
| | *Found* | *Calc.* | *Cr (VI)* | *Cl* | *Cr (VI)* | *Cl* |
| 1:2 | 31.0 | 30.9 | 16.4 | — | 16.1 | — |
| 1:1 | 34.0 | 33.9 | 23.5 | — | 23.4 | — |
| 2:1 | 36.0 | 35.7 | 14.8 | 10.4 | 15.1 | 10.3 |
| 4:1 | 37.5 | 37.2 | 8.63 | 18.4 | 8.81 | 18.0 |

additional lines at (Å) 3.16s, 2.22m and 1.81w corresponding[9] to those of KCl, whereas the residues of 1:2 molar ratios had $d_{hkl}$ values in addition to those of $K_2Cr_2O_7$, extra lines at (Å) 3.63m, 2.68s, 2.48s and 1.68s corresponding[9] to those of $Cr_2O_3$. The results of chemical, X-ray and IR analyses thus indicate that 1:1 molar ratios of $KClO_4$ and $CrO_3$, and $KClO_3$ and $CrO_3$ give $K_2Cr_2O_7$ as the decomposition product. The reaction schemes are given as,

$$xKClO_4 + yCrO_3 \rightarrow \tfrac{1}{2}K_2Cr_2O_7 + (x-1)KCl + \tfrac{1}{2}Cl_2 + (y-1)Cr_2O_3 + (2x-\tfrac{1}{2})O_2 \quad (1)$$

$$xKClO_3 + yCrO_3 \rightarrow \tfrac{1}{2}K_2Cr_2O_7 + (x-1)KCl + \tfrac{1}{2}Cl_2 + (y-1)Cr_2O_3 + (3x/2-\tfrac{1}{2})O_2 \quad (2)$$

$$x, y = 1, 2, 3 \ldots$$

Based on these schemes, the expected weight losses for different mixtures are calculated and the values are tabulated in Tables 1 and 2 together with the thermogravimetric results. The two results are in good agreement.

The DTA curves of $KClO_4$–$CrO_3$ mixtures (Fig. 1) showed an endotherm around 210°C due to the melting of $CrO_3$, an exotherm at 320°C assigned to the formation of $K_2Cr_2O_7$ and an endotherm at 400°C due to the melting of $K_2Cr_2O_7$.

An exotherm around 350°C followed by an endotherm at 470°C for 1:2 molar ratio is characteristic of the decomposition of $CrO_3$ present in excess, to the formation of $K_2Cr_2O_7$; the former is due to the expulsion of oxygen and the latter is due to the formation of $Cr_2O_3$. An endotherm at 300°C for 2:1 and 4:1 molar ratios is due to the phase transformation of unreacted $KClO_4$ and an endotherm immediately followed by an exotherm around 470°C is due to the decomposition of $KClO_4$. The DTA curves of the different molar ratios of $KClO_3$ and $CrO_3$ (Fig.2) showed an exotherm at 220°C due to the formation of $K_2Cr_2O_7$ and an endotherm at 400°C due to its melting. The 1:2 molar ratio showed an additional exotherm at 350°C and an endotherm around 470°C, which are characteristic of $CrO_3$ decomposition. In the case of 2:1 and 4:1 molar ratios there was an endothermic effect at 320°C ascribed to the melting of unreacted $KClO_3$ and exothermic effects at 350 and 380°C due to the decomposition of $KClO_3$.

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