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# The thermal decomposition of potassium bromate in the presence of chromium(III) oxide

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**Abstract**

The thermal behaviour of intimate mixtures of different mole ratios of potassium bromate and chromium(III) oxide has been studied using TG and DTA techniques in static air atmosphere. The products have been characterised by chemical analysis, infrared spectroscopy and X-ray diffraction studies. The studies indicate that $Cr_2O_3$ lowers the decomposition temperature of potassium bromate and is oxidised to Cr(VI). Each mole of Cr(III) takes up two moles of $KBrO_3$, to give potassium dichromate, and four moles of $KBrO_3$, to form potassium chromate.

*Keywords:* Chromium oxide; Decomposition; DTA; IRS; Potassium bromate; TG; XRD

## 1. Introduction

Processes involving chemical transformation of solids play an important role in modern technology as desired products may be formed by simple methods at low or moderate temperatures involving the reactions of precursory solids. The influence of metal oxides on the decomposition of halogen oxosalts has been studied in detail [1–8]. Thus, transition metal oxides with n- or p-type semiconducting behaviour are found to catalyse the decomposition of halogen oxosalts more effectively than rare-earth metal oxides by lowering the decomposition temperatures. However, $Al_2O_3$, $SiO_2$ and MgO, which are insulators, do not exhibit any catalytic influence [3] on the decomposition of halogen oxosalts. Furthermore,

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certain oxides chemically interact with the decomposition products to give new compounds [4–8]. In this paper, the solid state preparation of dichromate and chromate of potassium is described using a thermal decomposition method and $KBrO_3$ and $Cr_2O_3$ precursors. The decomposition studies were carried out by thermogravimetry and differential thermal analysis, and the decomposition products were characterised by chemical analysis, IR spectral measurements and X-ray diffraction patterns.

## 2. Experimental

The potassium bromate used was a commercially available analytical reagent grade sample. Chromium(III) oxide was prepared by heating the reagent grade hydrated chromium(III) nitrate at 500°C. Mixtures of $KBrO_3$ and $Cr_2O_3$ were prepared in 1:2, 1:1, 2:1, 3:1, 4:1, 6:1 and 8:1 mole ratios by taking the required amount and grinding them in an agate mortar for about 30 min until a satisfactory homogeneity of the mixture had been achieved.

The thermal decomposition studies (TG and DTA) were carried out on a Stanton Redcroft STA-780 series. Sample masses of approximately 3–5 mg were used for each analysis at a heating rate of 5°C $min^{-1}$. Constant temperature experiments were carried out in a muffle furnace in which the temperature could be controlled with an accuracy of $\pm 5$°C.

The chemical analyses of the products for bromide and Cr(VI) were followed by wet chemical processes. Thus, in a mixture of dichromate and $Cr_2O_3$, the two were separated by filtering the aqueous solution. Cr(VI) was determined by the iodometric method. The insoluble $Cr_2O_3$ was oxidised to Cr(VI) by sodium peroxide and determined as above. The mixture containing bromate and Cr(VI) was analysed by reducing it with sodium sulphite and a limited amount of dilute nitric acid to bromide and Cr(III), respectively. The bromide was precipitated as silver bromide and determined gravimetrically. Aqueous Cr(III) was oxidised to Cr(VI) by peroxide and determined iodometrically. Likewise, the mixture containing Cr(VI) and bromide was treated with sodium sulphite and a limited amount of dilute nitric acid. From this solution, Cr(III) and bromide were determined by following the above procedure.

IR spectra were measured using a Shimadzu 470 IR spectrophotometer using the KBr pellet technique. The X-ray powder diffraction patterns were taken with a Philips PW-1710 diffractometer using Cu K$\alpha$ radiation.

## 3. Results and discussion

The TG and DTA curves of $KBrO_3$ indicate that the compound melts at 410°C and decomposes in the temperature range 410–425°C, yielding KBr and $O_2$, in agreement with the reported [8] results of its thermal stability.

The TG curves of mixtures of $KBrO_3$ and $Cr_2O_3$ in different mole ratios are given in Fig. 1 and the TG data are listed in Table 1. The TG results suggest that the

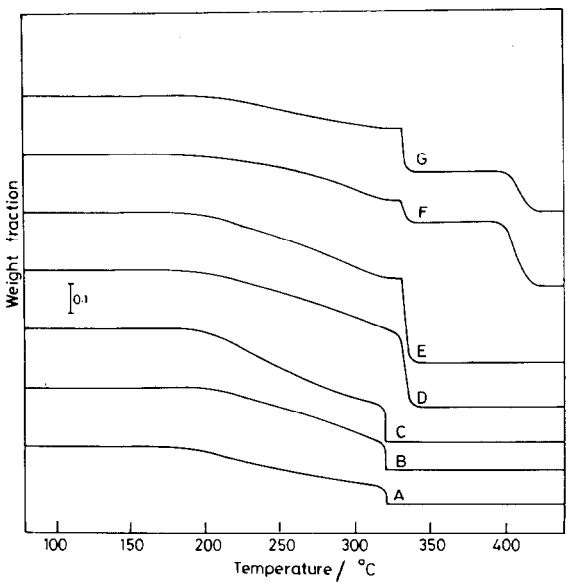


Fig. 1. TG plots of (A) 1:2, (B) 1:1, (C) 2:1, (D) 3:1, (E) 4:1, (F) 6:1, (G) 8:1 molar ratios of $KBrO_3$ and $Cr_2O_3$.

onset of the reaction occurs at 180°C for all the mixtures which is far below the decomposition temperature of free $KBrO_3$ [8]. The TG curves also suggest that the 1:2, 1:1 and 2:1 mole ratios of $KBrO_3$ and $Cr_2O_3$ decompose in a single state, the 3:1 and 4:1 ratios decompose in two stages, and the 6:1 and 8:1 mole ratios

Table 1
Thermogravimetric data for the decomposition of different mole ratios of potassium bromate and chromium(III) oxide

| Mole ratio $KBrO_3$:$Cr_2O_3$ | Temperature range/°C | Weight loss/% | |
|---|---|---|---|
| | | Found | Calcd. (based on Eq.) |
| 1:2 | 180–320 | 19.75 | 20.38 (3) |
| 1:1 | 180–320 | 29.03 | 30.09 (3) |
| 2:1 | 180–320 | 39.02 | 39.50 (1) |
| 3:1 | 180–340 | 47.19 | 47.75 (4) |
| 4:1 | 180–320 | 22.80 | 23.35 (5) |
| | 330–340 | 38.18 | 38.56 (6) |
| 6:1 | 180–320 | 16.11 | 16.62 (5) |
| | 330–340 | 23.84 | 24.92 (6) |
| | 410–425 | 13.79 | 13.28 |
| 8:1 | 180–320 | 12.5 | 12.87 (5) |
| | 330–340 | 16.7 | 18.51 (6) |
| | 410–425 | 19.43 | 18.78 |

Table 2
Analytical data for the residues of potassium bromate and chromium(III) oxide mixtures heated at different temperatures

| Mole ratio $KBrO_3$:$Cr_2O_3$ | Temperature/ °C | Cr(VI)/ % | Extent of Cr(VI) oxidation/% | $BrO_3^-$ | | $Br^-$ | |
|---|---|---|---|---|---|---|---|
| | | | | Found | Calcd. | Found | Calcd. |
| 1:2 | 320 | 11.00 | 24.90 | – | – | – | – |
| 1:1 | 320 | 16.21 | 49.69 | – | – | – | – |
| 2:1 | 320 | 21.35 | 99.95 | – | – | – | – |
| 3:1 | 340 | 15.91 | 99.87 | – | – | – | – |
| 4:1 | 320 | 12.68 | 99.92 | 25.21 | 25.46 | – | – |
| | 340 | 12.68 | 99.92 | – | – | – | – |
| 6:1 | 320 | 9.01 | 99.88 | 33.01 | 33.25 | – | – |
| | 340 | 9.01 | 99.88 | 23.00 | 22.14 | – | – |
| | 425 | 9.01 | 99.88 | – | – | 25.51 | 25.5 |
| 8:1 | 320 | 6.95 | 99.57 | 36.00 | 37.03 | – | – |
| | 340 | 6.95 | 99.57 | 30.10 | 30.29 | – | – |
| | 425 | 6.95 | 99.57 | – | – | 36.5 | 37.0 |

decompose in three stages. The temperature ranges of the three stages are 180–320, 330–340 and 410–425°C, respectively. Although, in all cases the decomposition begins at 180°C, there is a gradual weight loss up to about 320°C. However, a sudden weight loss appears at 320°C for the 1:2, 1:1, and 2:1 mixtures. The 4:1, 6:1 and 8:1 mixtures, after a gradual loss in weight from 180 to 320°C, reach a steady state in their weight loss curves up to 330°C; thereafter, appreciable weight loss occurs up to 340°C. The residues of mixtures 6:1 and 8:1 further decompose in the temperature range 410–425°C. The 3:1 mole ratio decomposes with gradual weight loss up to 320°C and then with an appreciable weight loss up to 340°C.

The analytical data of the chemical analyses are given in Table 2. The results indicate that the product of the decomposition of the 2:1 mole ratio mixture of $KBrO_3$ and $Cr_2O_3$ obtained at 320°C was found to contain only Cr(VI). However, analysis of the decomposition products of the 1:1 and 1:2 mole ratio mixtures indicated the presence of Cr(III) along with Cr(VI). The products of the decomposition of mole ratio mixtures higher than 2:1 at this temperature were found to contain Cr(VI) and excess bromate. However, at 425°C, the decomposition residue was found to be Cr(VI) and bromide.

The TG data and the results of the chemical analyses indicate that the products of the decomposition of the 2:1 mole ratio mixture obtained at 320°C, and of the 4:1 mole ratio mixture at 340°C, are $K_2Cr_2O_7$ and $K_2CrO_4$ respectively, according to reactions (1) and (2)

$$2KBrO_3 + Cr_2O_3 \rightarrow K_2Cr_2O_7 + Br_2 + O_2 \quad (1)$$

$$4KBrO_3 + Cr_2O_3 \rightarrow 2K_2CrO_4 + 2Br_2 + (7/2)O_2 \quad (2)$$

Also, the products of decomposition of 1:2 and 1:1 mixtures are $K_2Cr_2O_7$ and unreacted $Cr_2O_3$

$$KBrO_3 + xCr_2O_3 \rightarrow (1/2)K_2Cr_2O_7 + (x - (1/2))Cr_2O_3 + (1/2)Br_2 + (1/2)O_2 \qquad (x \geqslant 1) \tag{3}$$

As seen from Eq. (4), the 3:1 mole ratio mixture, however, gives a mixture of $K_2Cr_2O_7$ and $K_2CrO_4$ at 340°C in the ratio of 1:2

$$3KBrO_3 + Cr_2O_3 \rightarrow (1/2)K_2Cr_2O_7 + K_2CrO_4 + (3/2)Br_2 + (9/4)O_2 \tag{4}$$

The mole ratios 6:1 and 8:1 decompose to give $K_2CrO_4$ and unreacted $KBrO_3$ at this temperature; the latter decomposes to KBr and $O_2$ in the range 410–425°C which is the normal temperature of decomposition of free $KBrO_3$. The generalised reactions are given in Eqs. (5) and (6) where $y \geqslant 4$

$$yKBrO_3 + Cr_2O_3 \rightarrow K_2Cr_2O_7 + (y-2)KBrO_3 + Br_2 + O_2 \tag{5}$$

$$(y-2)KBrO_3 + K_2Cr_2O_7 \rightarrow 2K_2CrO_4 + (y-4)KBrO_3 + Br_2 + (5/2)O_2 \tag{6}$$

In a separate experiment, a 2:1 mole ratio of an intimate mixture of $KBrO_3$ and $K_2Cr_2O_7$ was subjected to thermogravimetric analysis. The mixture decomposed in the temperature range 325–340°C to form pure $K_2CrO_4$ as the final product, i.e. far below the temperature of decomposition of pure $KBrO_3$, thus suggesting that $K_2Cr_2O_7$ lowers the temperature of decomposition and interacts to form $K_2CrO_4$. This temperature is not much different from that found for the 4:1 mole ratio mixture of $KBrO_3$ and $Cr_2O_3$.

The IR spectrum of the products of decomposition of the 2:1 mole ratio mixture obtained at 320°C, showed absorption frequencies at 795(m), 880(m), 900(m), 920(w,sh) and 940(vs) $cm^{-1}$ which correspond to those of free $K_2Cr_2O_7$ [9], whereas the products of decomposition of 1:1 and 1:2 mixtures showed absorption frequencies at 620(m) and 550(w) $cm^{-1}$ due to $Cr_2O_3$ [10], in addition to those of $K_2Cr_2O_7$. The IR bands obtained at 860(s), 880(vs) and 935(s) $cm^{-1}$ in the spectrum of the decomposition products at 340°C of 4:1 mole ratio, correspond to those of free $K_2CrO_4$ [9]. However, the IR spectrum of the decomposition products of 3:1 mole ratio obtained at this temperature showed the characteristic frequencies of $K_2Cr_2O_7$ and $K_2CrO_4$ [9]. The residues of the 6:1 and 8:1 mole ratios heated to 340°C showed an additional IR frequency at 790(vs) $cm^{-1}$ due to $KBrO_3$ [9], but the IR spectra of the residues of these mixtures at 425°C showed bands due to $K_2CrO_4$ only.

Further comfirmation of the products at various stages of decomposition is obtained by X-ray powder diffraction patterns. The powder patterns of the decomposition products of 2:1 mole ratio mixture obtained at 320°C gave $d_{hkl}$ values of 3.28, 3.43, 3.53 and 3.61 Å which are in agreement with the pattern of free $K_2Cr_2O_7$ [11]. The powder patterns of the decomposition products of 1:1 and 1:2 mixtures gave $d_{hkl}$ values of $K_2Cr_2O_7$ and additional lines at 1.66, 2.63, 2.45 and 1.42 Å which are due to $Cr_2O_3$ [11]. The $d_{hkl}$ values obtained at 3.75, 3.25 and 3.03 Å for the decomposition product of the 4:1 mole ratio mixture at 340°C corresponds to those

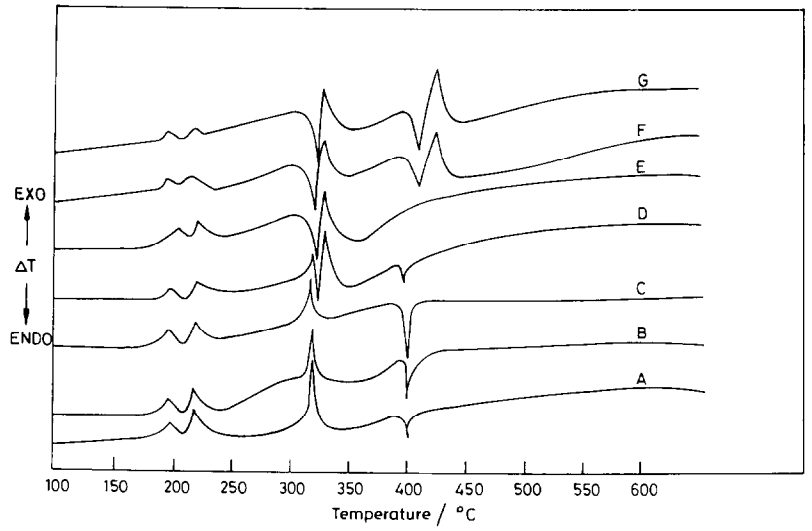


Fig. 2. DTA plots of (A) 1:2, (B) 1:1, (C) 2:1, (D) 3:1, (E) 4:1, (F) 6:1, (G) 8:1 molar ratios of $KBrO_3$ and $Cr_2O_3$.

of $K_2CrO_4$ [11]. However as observed from the IR data, the decomposition products of 3:1 mole ratio showed lines which are characteristic of $K_2Cr_2O_7$ and $K_2CrO_4$ [11]. The X-ray powder patterns of higher mixtures at this temperature gave patterns corresponding to that of $K_2CrO_4$ and additional lines at 3.21, 3.01, 4.36 and 2.20 Å which are due to unreacted $KBrO_3$ [11]; but the products obtained at 425°C gave $d_{hkl}$ values characteristic of $K_2CrO_4$ with additional lines at 3.31, 2.32, 1.90 and 1.46 Å due to KBr.

The DTA plots of all the mixtures are given in Fig. 2. The curves show two exothermic peaks at around 190 and 220°C that are attributed to the evolution of $Br_2$. In order to verify the evolved gas as bromine, a separate experiment was performed as follows. The mixtures of $KBrO_3$ and $Cr_2O_3$ were heated gradually from room temperature and the evolved gas was collected by absorption in water, and confirmed as bromine.

The exotherm observed at 320°C for mixtures of 2:1 and lower mole ratios is due to the formation of $K_2Cr_2O_7$ and the endotherm at 395°C is due to the melting of $K_2Cr_2O_7$ [12]. The endotherm at 325°C followed by an exotherm at 330°C for the decomposition of 4:1 mole ratio is ascribed to the decomposition of $K_2Cr_2O_7$ to form $K_2CrO_4$. The mixtures of 6:1 and 8:1 showed an endotherm at 410°C and exotherm at 425°C which are characteristic of melting followed by the decomposition of free $KBrO_3$.

## 4. Conclusions

The results of the investigation suggest that $Cr_2O_3$, a p-type semi-conductor, undergoes an electron transfer process during the decomposition of $KBrO_3$, result-

ing in the formation of $CrO_3$ which combines with $K_2O$, the initial decomposition product of $KBrO_3$, to form chromates(VI). Thus the reaction of one mole of $Cr_2O_3$ with two moles of $KBrO_3$ results in the formation of $K_2Cr_2O_7$ at 320°C. With increase in $KBrO_3$ content, the dichromate formed converts itself into chromate and four moles of $KBrO_3$ react with one mole of $Cr_2O_3$ at 340°C to yield two moles of $K_2CrO_4$. Thus $Cr_2O_3$ lowers the decomposition temperature of $KBrO_3$ from 410 to 180°C, is oxidised to Cr(VI), and abstracts $K_2O$ to form chromates.

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