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Solid state reactions in the system oxalate–bromate–chromium(III) oxide

U.S. Shoba, M.R. Udupa *

Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

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Abstract

The TG and DTA techniques in static air atmosphere have been employed to study the thermal behaviour of intimate mixtures comprising different mole ratios of potassium oxalate, potassium bromate and chromium(III) oxide. The products are characterised by chemical analysis, infrared spectroscopy and X-ray diffraction studies. The studies indicate that the onset of the reaction occurs after the dehydration of potassium oxalate around 200°C. Also it suggests that the chromium(III) oxide initiates the decomposition of potassium bromate at a lower temperature resulting in the liberation of oxygen which is utilised in the oxidative decomposition of potassium oxalate. With the stoichiometric amounts (3:3:1 molar ratio) of potassium bromate, potassium oxalate and chromium(III) oxide the reaction gives rise to a mixture of potassium chromate, potassium carbonate and potassium bromide in the molar ratio of 2:2:1.

Keywords: Chromium oxide; DTA; IRS; Potassium bromate; Potassium oxalate; TG; XRD

1. Introduction

Solid state science is concerned with the synthesis, structure, properties and application of solid materials. Thermal analysis finds application in solid state chemistry by characterising compounds using thermogravimetric analysis, differential thermal analysis and related thermal techniques. These methods study properties and processes such as phase transitions and mechanisms of thermal decomposition and solid state reactions. The influence of metal oxides on the thermal decomposition of halogen oxosalts in the solid state has been studied extensively. The catalytic effect of 23

* Corresponding author.

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different metal oxides on the decomposition of molten potassium chlorate has been reported by Iwakura et al. [1]. The oxide α-Al_2O_3 was found to lower the melting and decomposition temperatures of $KBrO_3$, and α-Fe_2O_3 remarkably lowered the decomposition of $KBrO_3$ from 425 to 260°C [2]. Chromium(III) oxide was found to reduce the decomposition temperatures of $NaClO_3$ [3], $KClO_3$ [4] and $KBrO_3$ [5] and chemically interacts with the decomposed product to yield Cr(VI) compounds. This paper reports the results of a study of the solid state reactions occurring in the system potassium oxalate–potassium bromate–chromium(III) oxide. These studies used thermogravimetry and differential thermal analysis, and the products were characterised by chemical analysis, IR spectral measurements and X-ray diffraction patterns.

2. Experimental

The potassium bromate and potassium oxalate used were commercially available analytical reagent grade samples. Chromium(III) oxide was prepared by heating reagent grade hydrated chromium(III) nitrate at 500°C. Mixtures of $K_2C_2O_4 \cdot H_2O$, $KBrO_3$ and Cr_2O_3 were prepared in different molar ratios by taking the required amounts of the reactants and mixing and grinding them in an agate mortar for about 30 min until satisfactory homogeneity of the mixture had been achieved.

A Stanton Redcroft STA-780 system was used for thermal decomposition studies. Sample masses of approximately 3–5 mg were used for each analysis at a heating rate of $10°C\,min^{-1}$. To characterise the intermediates formed and the final product of decomposition, the reaction mixture was heated at a desired temperature in a muffle furnace in which the temperature could be controlled with an accuracy of $\pm$ 5°C.

The chemical analyses of the products containing bromate, bromide, Cr(VI), Cr_2O_3 and carbonate were conducted by wet chemical processes. Thus in a mixture containing Cr(VI), bromide and carbonate, Cr(VI) was determined by an iodometric method. The bromide was precipitated as silver bromide and was determined gravimetrically after reducing Cr(VI) to Cr(III) by sodium sulphite with a limited amount of dil. HNO_3. The carbonate was determined titrimetrically using methyl orange as the indicator. In the mixture containing Cr_2O_3, Cr(VI), bromide and carbonate, Cr_2O_3 was separated by filtration and was determined by an iodometric method after oxidising to Cr(VI) using Na_2O_2. The mixtures containing bromate in addition to the other products were treated with sodium sulphite and a limited amount of dil. HNO_3 to convert the bromate to bromide.

The IR spectra were measured with a Shimadzu 470-IR Spectrophotometer using the KBr pellet technique. The X-ray powder diffraction patterns were obtained with a Philips PW-1710 diffractometer using CuKα radiation.

3. Results and discussion

The TG and DTA curves of $K_2C_2O_4 \cdot H_2O$ indicate that the compound undergoes dehydration in the temperature range 100–140°C with a crystallographic phase

transition at 400°C. The results are in accordance with reported values [6]. In the temperature range 480–550°C it decomposes to K_2CO_3. On the other hand $KBrO_3$ melts at 410°C and decomposes to KBr and O_2 in the temperature range 410–425°C; this is in agreement with reported [2] results of its thermal stability.

The TG curves of mixtures of $K_2C_2O_4 \cdot H_2O$, $KBrO_3$ and Cr_2O_3 in different molar ratios are given in Fig. 1 and the TG data are tabulated in Table 1. The TG results suggest that the dehydration of $K_2C_2O_4 \cdot H_2O$ in the mixture occurs in the temperature range 100–140°C and that the onset of the decomposition reaction occurs at 200°C for all the mixtures. This is far below the temperature of decomposition of either $KBrO_3$ [2] or dehydrated $K_2C_2O_4$ [6]. The TG curves also suggest that the weight loss occurs

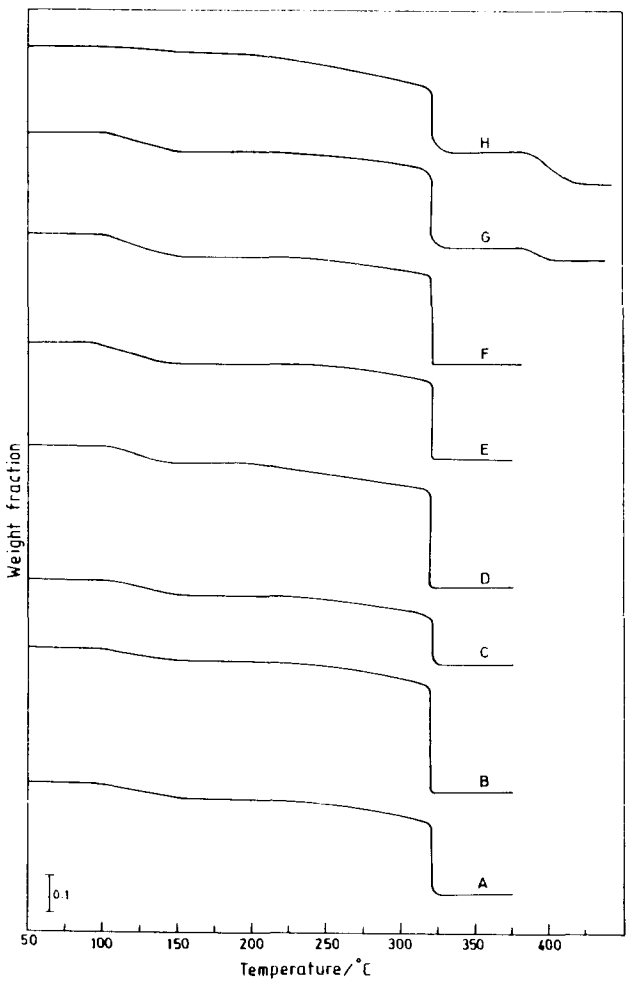

Fig. 1. TG plots of (A) 1:1:1, (B) 1:2:1, (C) 2:1:1, (D) 2:2:1, (E) 3:2:1. (F) 3:3:1, (G) 3:4:1 and (H) 1:4:1 molar ratios of $K_2C_2O_4 \cdot H_2O$, $KBrO_3$ and Cr_2O_3.

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

Molar ratio $K_2C_2O_4 \cdot H_2O$: $KBrO_3$:Cr_2O_3	Temperature range/°C	Weight loss/%	
		Found	Calcd. (based on Eq.)
1:1:1	100–140	3.37	3.25
	200–340	25.46	24.93(2)
1:2:1	100–140	2.87	2.69
	200–340	36.87	37.03(2)
2:1:1	100–140	4.00	4.21
	200–340	19.44	19.54(2)
2:2:1	100–140	4.12	4.44
	200–340	32.69	29.98(2)
3:2:1	100–140	5.05	5.20
	200–340	26.08	25.36(2)
3:3:1	100–140	5.20	4.50
	200–340	30.37	31.94(1)
3:4:1	100–140	4.21	3.90
	200–340	27.89	26.62(3)
	370–420	5.64	5.24
1:4:1	100–140	1.74	1.79
	200–340	27.72	28.35(3)
	370–420	11.35	11.32

in a sluggish manner up to 320°C for all the mixtures. Thereafter there is a sudden drop in weight. The reaction is complete at 340°C for all the mixtures containing a limited amount of $KBrO_3$. However, for the molar ratios with higher bromate contents the decomposition of unreacted $KBrO_3$ takes place in the temperature range 380–420°C.

The analytical data for the products of decomposition at 340°C reveal that the decomposition product of the 3:3:1 molar ratio contains Cr(VI), bromide and carbonate whereas those for the 1:1:1, 1:2:1, 2:1:1, 2:2:1 and 3:2:1 ratios contain unreacted Cr_2O_3 in addition to Cr(VI), bromide and carbonate. The analyses of the products for ratios containing excess bromate beyond that of a 3:3:1 ratio reveal the presence of unreacted bromate at this temperature in addition to the products mentioned above. At 420°C the product contains no bromate. The analytical data are summarised in Table 2.

The results obtained from the TG data and the analytical data indicate that the product of decomposition of 3:3:1 molar ratio at 340°C is according to Eq. (1)

$$3K_2C_2O_4 + 3KBrO_3 + Cr_2O_3 \rightarrow 2K_2CrO_4 + 2K_2CO_3 + KBr + 4CO_2\uparrow + O_2\uparrow + Br_2\uparrow \quad (1)$$

Table 2
Analytical data of the residues of potassium oxalate, potassium bromate and chromium(III) oxide mixture heated at different temperatures

Molar ratio	Temp./°C	Cr(VI)/%	Extent of Cr(VI) oxidn/%	BrO_3^-/%		Br^-/%		CO_3^{2-}/%	
				Found	Calcd.	Found	Calcd.	Found	Calcd.
1:1:1	340	9.56	33.00	–	–	7.25	7.36	12.00	11.65
1:2:1	340	21.05	83.00	–	–	6.55	6.47	2.40	2.47
2:1:1	340	3.31	16.60	–	–	10.10	10.18	21.60	20.96
2:2:1	340	8.47	66.50	–	–	9.30	9.31	13.05	13.95
3:2:1	340	7.08	49.80	–	–	10.85	10.88	19.51	20.42
3:3:1	340	13.03	99.70	–	–	10.15	10.21	16.00	15.31
3:4:1	340	10.50	99.50	7.95	8.41	8.35	8.41	11.80	12.59
	420	11.30	99.50	–	–	17.65	17.72	13.85	13.29
1:4:1	340	15.01	99.90	18.15	18.97	3.75	3.77	–	–
	420	16.31	99.90	–	–	25.45	25.54	–	–

The generalised reaction for the decomposition of 1:1:1, 1:2:1, 2:1:1, 2:2:1 and 3:2:1 molar ratios is represented by Eq. (2)

$$xK_2C_2O_4 + yKBrO_3 + Cr_2O_3 \rightarrow ((7x - 3y)/6)K_2CO_3 + (x/3)KBr + ((3y - x)/3)K_2CrO_4 + ((5x + 3y)/6)CO_2\uparrow + ((3y - x)/6)Br_2\uparrow + ((3y - x)/6)O_2\uparrow + ((6 - 3y + x)/6)Cr_2O_3 \quad (2)$$

$x = 1, 2, 3; \quad y = 1, 2$

The decomposition reaction for bromate-rich mixtures at 340°C is represented by Eq. (3) and the unreacted bromate decomposes to KBr and O_2 in the range 380–420°C.

$$xK_2C_2O_4 + yKBrO_3 + Cr_2O_3 \rightarrow (x - 1)K_2CO_3 + (x/3)KBr + 2K_2CrO_4 + (x + 1)CO_2\uparrow + Br_2\uparrow + O_2\uparrow + (y - (x/3) - 2)KBrO_3 \quad (3)$$

$x \leq 3, \quad y \geq 3$

The IR spectrum of the decomposition product of the 3:3:1 molar ratio at 340°C showed absorption frequencies at 935(s), 875(vs) and 855(w, sh) cm^{-1} due to K_2CrO_4, and 1450(vs), 865(m) and 700(m) cm^{-1} which correspond to those of K_2CO_3 [7]. The products of decomposition of the 1:1:1, 1:2:1, 2:1:1, 2:2:1 and 3:2:1 molar ratios showed absorption frequencies at 635(m), 560(m) and 440(w) cm^{-1} that are due to Cr_2O_3 [8] in addition to those of K_2CrO_4 and K_2CO_3. The IR spectra of the decomposition products of bromate-rich ratios at 340°C displayed a medium intensity band at 790 cm^{-1} due to $KBrO_3$ [7], in addition to the bands due to K_2CrO_4 and carbonate. However the product obtained at 420°C for these ratios showed no absorption frequency at 790 cm^{-1} as the bromate had decomposed to KBr.

Further confirmation of the products at various stages of decomposition was obtained by X-ray powder diffraction patterns. The powder patterns for the decompo-

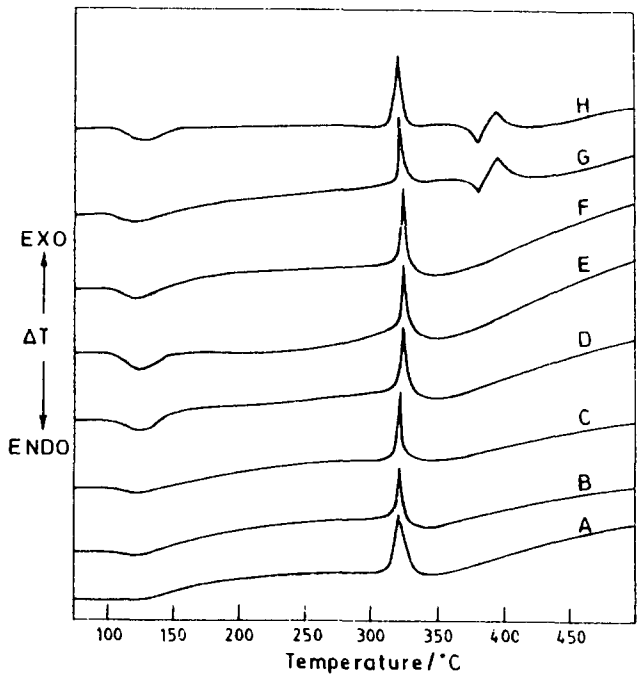

Fig. 2. DTA plots of (A) 1:1:1, (B) 1:2:1, (C) 2:1:1, (D) 2:2:1, (E) 3:2:1, (F) 3:3:1, (G) 3:4:1 and (H) 1:4:1 molar ratios of $K_2C_2O_4 \cdot H_2O$, $KBrO_3$ and Cr_2O_3.

sition product of the 3:3:1 molar ratio obtained at 340°C gave d_{hkl} values at 3.05, 2.97, 2.92 and 2.62 Å due to K_2CrO_4; 2.99, 2.82, 2.79 and 2.39 Å due to K_2CO_3 and 3.32, 2.35, 1.98 and 1.48 Å due to KBr [9]. The products of decomposition for the 1:1:1, 1:2:1, 2:1:1, 2:2:1 and 3:2:1 molar ratios showed additional lines at 2.65, 2.45 and 1.66 Å which are ascribed to Cr_2O_3 [9]. Additional d_{hkl} values observed at 4.39, 3.20, 3.01 and 2.20 Å for the products of bromate-rich mixtures at 340°C were due to $KBrO_3$ which were absent in the products obtained at 420°C.

The DTA plots for all the mixtures are given in Fig. 2. An endotherm observed at 120°C was due to the dehydration of $K_2C_2O_4 \cdot H_2O$. The sharp exotherm at 315°C for all the molar ratios corresponded to the oxidation reaction. The bromate-rich mixtures exhibited an endotherm at 380°C followed by an exotherm at 390°C ascribed to melting followed by the decomposition of $KBrO_3$.

4. Conclusion

The onset of the reaction occurs after dehydration of the potassium oxalate at around 200°C. The chromium(III) oxide initiates the decomposition of potassium bromate at a lower temperature resulting in the evolution of oxygen. This oxygen

immediately initiates the oxidative decomposition of potassium oxalate. Normally the oxidative decomposition of oxalate in presence of bromate occurs at a higher temperature range of 285–375°C. However, in presence of chromium(III) oxide the reaction proceeds at a lower temperature leading to the simultaneous reaction of the potassium bromate with chromium(III) oxide and potassium oxalate.

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