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THERMOCHEMICAL INVESTIGATION OF SOLID STATE REACTIONS IN MOLYBDATES/TUNGSTATES SYSTEM

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Abstract

Investigation on the influence of MoO_3 and WO_3 on the thermal decomposition of the halogen oxysalts, $KClO_4$, $KClO_3$, $KBrO_3$ and KIO_3 has been followed by TG, DTA, IR spectroscopy and X-ray diffraction studies. The results suggest the formation of mono-, di-, tri- and tetra- molybdates/tungstates in solid state by the reaction of appropriate mole ratios of the reactants.

Introduction

The catalytic influence of transition metal oxides on the decomposition of halogen oxysalts is of considerable interest [1] because the decomposition of these compounds is extremely sensitive to the presence of additives and they also serve as practical sources of oxygen. In the present study, the influence of MoO_3 and WO_3 on the thermal decomposition of halogen oxysalts has been done. Detailed studies on the influence of Cr_2O_3 in the decomposition of perchlorates and chlorates [2,3] have been made. The studies were followed by thermogravimetry (TG), differential thermal analysis (DTA) and constant temperature heating experiments and the products of the reactions were characterised by chemical analyses, X-ray powder diffraction and infrared spectral studies.

Experimental

The reaction mixtures of $KClO_4$-MoO_3, $KClO_3$-MoO_3/WO_3, $KBrO_3$-MoO_3/WO_3 and KIO_3-MoO_3/WO_3 were made in different mole ratios of 1:3, 1:2, 2:3, 1:1, 2:1 and 3:1 by intimate mixing and grinding of the reactants.

A Stanton simultaneous thermal analyser 780 was employed for TG and DTA studies in static air. The rate of heating was kept at 10^o/min. Constant temperature heating experiments were carried out in a temperature controlled furnace.

IR spectra were recorded in the range 2000 - 400 cm^{-1} with a Perkin-Elmer 983 spectrophotometer employing KBr pellet technique. The X-ray powder diffraction patterns were recorded in a Philips diffractometer using CuK_α radiation.

The kinetics of the reactions were followed by using a modified computer program of Reich and Stivala [4] to arrive at a possible mechanism and the energy of activation values of the reaction.

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Results and Discussion

The thermal behaviour of the halates is similar to the reported data [5] with the formation of metal halides as the end products. The decomposition temperatures of $KClO_4$, $KClO_3$, $KBrO_3$ and KIO_3 are 540, 360, 382 and 560°C and the iodates are the most stable.

$KClO_4$-MoO_3

Representative curves for TG and DTA of the reaction mixtures Fig.(1) indicate a single step weight loss in all the mixtures. The rate of weight loss is initially slower and becomes faster towards the end of the reaction. The endotherm at 300°C observed in the DTA curves of all the mixtures is due to the orthorhombic to cubic phase transition of $KClO_4$, temperature of which is not influenced by the presence of MoO_3 and the endotherm at 540°C is due to the melting of $KClO_4$. The reaction between $KClO_4$ and MoO_3 manifests as an exotherm in all the mixtures except in 1:3 mole ratio where the reaction is complete very fast. The endotherm at 557° in 1:2 and 1:3 mixtures is due to the melting of the product, $K_2Mo_4O_{13}$.

The products of decomposition of 2:1 and 3:1 mole ratios were partly soluble in water and contained KCl, while the products from 1:3 and 1:2 were insoluble and that from 1:1 contained traces of KCl.

The X-ray powder diffraction pattern of the residues of 1:3 and 1:2 mixtures had the following intense d_{hkl} values (Å): 6.87, 3.52, 3.28, 2.96, 2.832 which correspond to $K_2Mo_4O_{13}$ [6] that of 1:1 ratio had the d_{hkl} values 5.98, 3.47, 3.33, 3.30, 3.12 due to $K_2Mo_2O_7$ and those of 2:1 and 3:1 mixtures give d_{hkl} (5.53, 4.74, 3.11, 2.99); (5.18, 3.25, 2.87, 1.72) and (3.15, 2.23, 1.82, 1.55) due to K_2MoO_4, MoO_3 and KCl respectively.

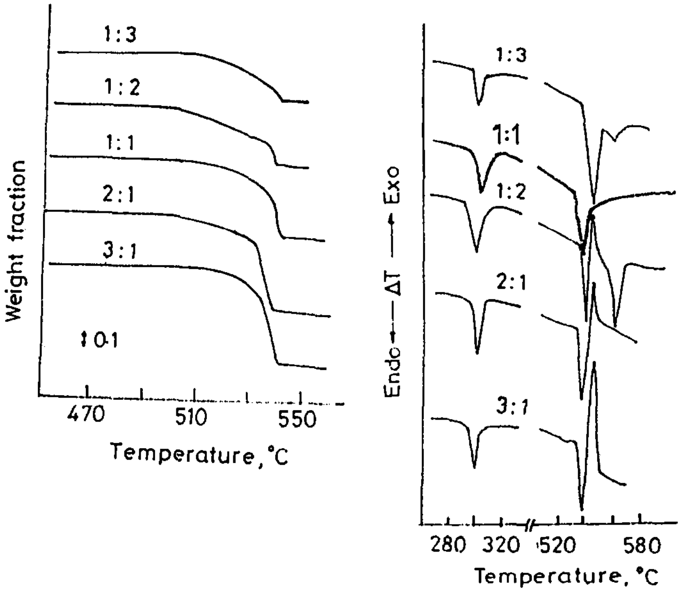

Fig. 1 TG and DTA curves of $KClO_4$ - MoO_3 mixtures

Further confirmation of the products of decomposition has been arrived at by the IR spectroscopy. The infrared spectra of the products from 1:3 and 1:2 ratios correspond to $K_2MoO_4O_{13}$ [7] with bands at 960m, 945s, 935m, 920s, 901s, 890s, 868s, 755s, 622s, 580s, 550s, 518s, 470m and 431m cm^{-1} while the product from 1:1 mixture shows absorptions corresponding to $K_2MO_2O_7$ at 930m, 905s, 870s, 720s, 703s, 570w, 480m and 402m cm^{-1}. A single broad band at 840 cm^{-1} characterising K_2MoO_4 is split by the presence of MoO_3 and KCl and additional bands are observed at 920, 860 and 670 cm^{-1}.

Based on the results of the above analyses, the reaction schemes could be proposed as:

$$KClO_4 + xMoO_3 \rightarrow 1/2\ K_2MO_4O_{13} + (x-2)MoO_3 + 1/2\ Cl_2 + 7/4\ O_2 \quad x=2,3,...$$

$$KClO_4 + MoO_3 \rightarrow 1/2\ K_2MO_2O_7 + 1/2\ Cl_2 + 7/4\ O_2$$

$$KClO_4 + MoO_3 \rightarrow 1/2\ K_2MoO_4 + 1/2\ MoO_3 + (y-1)KCl + 1/2\ Cl_2 + (2y - 1/4)O_2 \quad y=2,3,....$$

Table 1. Percentage weight loss from the TG of $KClO_4$-MoO_3 mixtures

$KClO_4$-MoO_3 mole ratio		1:3	1:2	1:1	2:1	3:1
Weight loss	Found	14.44	20.11	30.20	36.06	38.42
	Calcd	15.95	21.34	32.21	36.81	39.13

The weight loss calculated on the basis of the reactions proposed are found to agree well with those observed (Table 1).

KXO_3-MoO_3

The reactions of the other halates, $KClO_3$, $KBrO_3$ and KIO_3 with MoO_3 have been generalised and tabulated in Table 2, since the basic reactions in various ratios are the same in all the three systems. The end products have been confirmed by IR and X-ray diffraction studies.

Mixtures in each of the three systems undergo a single step reaction in the temperature range indicated. The reactions begin at a temperature much lower than the decomposition temperature of either of the reactants and also the reactions occur much faster when the proportion of MoO_3 is greater in the reaction mixture. These clearly point out that MoO_3 exerts a catalytic effect on the reaction but to a lesser extent [8] than that of Cr_2O_3. Moreover, since the reactions are completed faster in higher ratios of MoO_3, the DTA peak pattern is also simpler in mixtures like 1:3 and 1:2 and becomes gradually complicated in ratios of 2:1 and 3:1. Thus, in the system $KClO_3$-MoO_3, the reaction occurs with just one exotherm in 1:3, two exotherms in 1:2 and two exotherms and an endotherm in 1:1, 2:1 and 3:1. Similar behaviour is observed in KIO_3-MoO_3 system. In all the mixtures of $KBrO_3$-MoO_3, the reactions occur with an endothermic peak followed by an exothermic effect.

Table 2 : TG and DTA data of $KClO_3$, $KBrO_3$, KIO_3 - MoO_3 mixtures

KXO_3-MoO_3 Mole Ratio	Reaction Scheme proposed	$KClO_3$	$KBrO_3$	KIO_3
1:3	$KXO_3 + 3MoO_3 \rightarrow \frac{1}{2}K_2Mo_4O_{13} + MoO_3 + \frac{1}{2}X_2 + 5/4\ O_2$	(a) 330 - 355 (b) 12.11%; 13.5% (c) (+)341, (-)540, (-)557	260 - 380 21.89%; 20.03% (-)380, (+)384, (-)557	435 - 475 24.70%; 25.85% (-)435, (-)557
1:2	$KXO_3 + 2MoO_3 \rightarrow \frac{1}{2}K_2Mo_4O_{13} + \frac{1}{2}X_2 + 5/4\ O_2$	(a) 335 - 360 (b) 17.25%; 18.26% (c) (+)336, (+)342, (-)540, (-)557	270 - 385 26.59%; 26.37% (-)380, (+)384, (-)557	435 - 480 32.70%; 33.27% (-)435, (-)453, (-)557
2:3	$2KXO_3 + 3MoO_3 \rightarrow K_2Mo_3O_{10} + X_2 + 5/4\ O_2$	(a) 320 - 370 (b) 21.42%; 22.15% (c) (+)336, (-)346,	270 - 385 31.76%; 31.07% (-)380, (+)384,	440 - 505 38.89%; 38.84% (-)435, (-)455
1:1	$KXO_3 + MoO_3 \rightarrow \frac{1}{2}K_2Mo_2O_7 + \frac{1}{2}X_2 + 5/4\ O_2$	(a) 330 - 390 (b) 27.45%; 28.13% (c) (+)341, (+)364, (-)346	270 - 385 37.51%; 38.26% (-)380, (+)384,	440 - 505 45.65%; 46.65% (-)435, (-)452, (-)470
2:1	$2KXO_3 + MoO_3 \nearrow$ (i) $K_2MoO_4 + X_2 + 5/2O_2$ $\searrow$ (ii) $\frac{1}{2}K_2MoO_4 + \frac{1}{2}MoO_3 + KX + \frac{1}{2}X_2 + 11/4\ O_2$	(a) (ii) 325 - 410 (b) 30.01%; 31.60% (c) (+)330, (+)370, (-)349	(i) 270-385 48.43%; 49.79% (-)380, (+)384,	(i) 440 - 525 58.05%; 58.38% (-)452, (+)463, (+)470
3:1	$3KXO_3 + MoO_3 \nearrow$ (i) $K_2MoO_4 + KX + X_2 + 4\ O_2$ $\searrow$ (ii) $\frac{1}{2}K_2MoO_4 + \frac{1}{2}MoO_3 + 2KX + \frac{1}{2}X_2 + 17/4\ O_2$	(a) (ii) 325 - 420 (b) 32.81%; 33.41% (c) (+)330, (+)370, (-)349	(i) 270-385 44.14%; 44.34% (-)380, (+)384,	(i) 440 - 600 47.72%; 48.59% (-)452, (+)463, (+)471, (-)562

(a) Temp. range of reaction (°C); (b) Weight loss-observed; Calculated (c) DTA peak maxima (°C)
(-) Endotherm; (+) Exotherm

Table 3 : TG and DTA data of $KClO_3$, $KBrO_3$, KIO_3 - WO_3 mixtures

KXO_3-WO_3 Mole Ratio	Reaction Scheme proposed	$KClO_3$	$KBrO_3$	KIO_3
1:3	$KXO_3 + 3WO_3 \rightarrow \frac{1}{2}K_2W_4O_{13} + WO_3 + \frac{1}{2}X_2 + 5/4\ O_2$	(a) 330 - 435 (b) 8.06%; 9.23% (c) (-)342,(+)353,	250 - 395 13.95%; 13.91% (-)351,(+)358	450 - 535 16.81%; 18.36% (-)512
1:2	$KXO_3 + 2WO_3 \rightarrow \frac{1}{2}K_2W_3O_{10} + \frac{1}{2}WO_3$ $\frac{1}{2}X_2 + 5/4\ O_2$	(a) 330 - 435 (b) 11.35%; 12.88% (c) (-)342;(+)353	270 - 395 19.07%; 19.03% (-)360,(+)365,	450 - 535 23.74%; 24.65% (-)512
2:3	$2KXO_3 + 3WO_3 \rightarrow K_2W_3O_{10} + X_2 + 5/2\ O_2$	(a) 330 - 435 (b) 13.67%; 16.05% (c) (-)342,(-)353	275 - 398 21.52%; 23.31% (-)360,(+)365	450 - 540 28.31%; 29.73% (-)512
1:1	$KXO_3 + WO_3 \rightarrow \frac{1}{2}K_2W_2O_7 + \frac{1}{2}X_2 + 5/4\ O_2$	(a) 330 - 435 (b) 15.60%; 21.30% (c) (-)342,(+)353,	275 - 398 29.58%; 30.09% (-)372,(+)375	450 - 540 37.47%; 37.46% (-)505,(-)514
2:1	$2KXO_3 + WO_3$ ↗ (i) $K_2WO_4 + X_2 + 5/2\ O_2$ ↘ (ii) $\frac{1}{2}K_2WO_4 + \frac{1}{2}WO_3 + KX + \frac{1}{2}X_2 + 11/4\ O_2$	(a) (ii)320 - 520 (b) 24.93%;25.89% (c) (-)342,(+)360, (+)410	290-385 36.07%;(i)42.06% (ii)29.52% (-)365,(+)371	450 - 610 45.14%;(i)50.62% (ii)57.75% (-)508, (-)535
3:1	$3KXO_3 + WO_3$ ↗ (i) $K_2WO_4 + KX + X_2 + 4\ O_2$ ↘ (ii) $\frac{1}{2}K_2WO_4 + \frac{1}{2}WO_3 + 2KX + \frac{1}{2}X_2 + 17/4\ O_2$	(a) (ii)320 - 520 (b) 27.84%;28.52% (c) (-)342,(+)360, (+)410	290-395 35.83%;(i)39.30% (ii)29.34% (-)372, (+)375	440 - 610 41.16%;(i)43.72% (ii)30.10% (-)510, (-)540

(a) Temp. range of reaction (°C); (b) Weight loss-observed; Calculated (c) DTA peak maxima (°C)
(-) Endotherm; (+) Exotherm

The weight losses observed for the reactions agree with the values calculated on the basis of reaction schemes proposed (Table 2). In 2:1 and 3:1 mole ratios, while $KBrO_3$ and KIO_3 give K_2MoO_4, $KClO_3$ gives a mixture of K_2MoO_4, KCl and MoO_3 as the end product. This is probably because the temperature range of the reaction in $KClO_3$-MoO_3 mixtures overlaps well with the decomposition temperature range of $KClO_3$ and hence a part of $KClO_3$ decomposes to KCl before the completion of the reaction.

KXO_3-WO_3

The results, from all the three systems (Table 3), indicate that either the temperature range of the reaction is increased and/or shifted to higher regions of temperature compared to MoO_3 systems and that the 1:2 mixture gives only the tritungstate as the product and not the tetratungstate. These clearly point out that WO_3 is much less catalytically reactive compared to MoO_3. As a consequence, the reactions occur at higher temperatures and near the decomposition temperature of the halates making the reaction process more complex in higher ratios of 2:1 and 3:1. Thus weight losses do not quite correspond to stoichiometric reaction schemes. But the chemical analysis, IR spectra and the X-ray diffraction patterns of the products indicate the presence of the proposed products. The DTA curves show an endotherm followed by an exotherm for the reaction in all the mixtures of $KBrO_3$ and 1:3, 1:2, 2:3 and 1:1 mixtures of $KClO_3$-WO_3. An additional exotherm is observed in 2:1 and 3:1 mixtures of the latter system. In the KIO_3-WO_3 system, the reaction is manifested as an endotherm in 1:3, 1:2 and 2:3 mixtures and two endotherms in 1:1 2:1 and 3:1 mole ratios.

Kinetics

The kinetics of the reaction was followed for all the mixtures in KIO_3-MoO_3 system and the reactions were found to follow the Avrami-Erofeev type of nuclei growth mechanism [9] and the energy of activation values 20 Kcal/mol was obtained for all the ratios indicating that the same mechanism is operative in all the reactions.

Conclusion

The presence of MoO_3, while catalysing the decomposition of the potassium halates opens up a new route to the synthesis of polymolybdates in solid state. WO_3 being less reactive, catalyses the decomposition of halates to a lesser extent compared to MoO_3. The reactions leading to the formation of polytungstates are also not facile, requiring prolonged heating at higher temperatures.

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