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Thermal Behaviour of Potassium Perchlorate-Chromium(III) Nitrate & Potassium Chlorate-Chromium(III) Nitrate Mixtures

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Thermal decomposition of intimate mixtures of different molar ratios of potassium perchlorate and chromium(III) nitrate, and of potassium chlorate and chromium(III) nitrate has been studied employing thermogravimetry and differential thermal analysis. The decomposition products have been examined by chemical analysis, infrared spectroscopy and X-ray powder diffraction analysis. Upon heating the 1 : 1 mixture of potassium perchlorate and chromium(III) nitrate to 380° and that of potassium chlorate and chromium(III) nitrate to 300°, Cr(III) is completely oxidized to potassium dichromate. Only a stoichiometric amount of Cr(III) is oxidized from the 1 : 2 mixture leaving behind the unoxidized Cr(III) as Cr_2O_3, whereas from the mixtures greater than 1 : 1, Cr(III) is completely oxidized and the excess $KClO_4$ and $KClO_3$ decomposed around 400° and 300° respectively which are much below the decomposition temperatures of pure $KClO_4$ and $KClO_3$.

RECENTLY Udupa[1,2] made detailed studies on the thermal decomposition of $KClO_4$ and $KClO_3$ in the presence of Cr_2O_3 and observed that Cr_2O_3 not only lowered the decomposition temperatures but also reacted chemically to form $K_2Cr_2O_7$; each mole of Cr_2O_3 takes up two moles of $KClO_4$ and 8/3 moles of $KClO_3$. The oxidation of Cr(III) is attributed to the abstraction of oxygen from the perchlorate and the chlorate moieties. In continuation of this work[1,2] we report here the thermal benaviour of $KClO_4$-$Cr(NO_3)_3.9H_2O$ and $KClO_3$-$Cr(NO_3)_3.9H_2O$ mixtures. The studies are followed by thermogravimetry, differential thermal analysis, chemical analysis, X-ray powder diffraction patterns and infrared spectral analysis.

Materials and Methods

$KClO_4$ used was BDH (London) and $9H_2O.Cr(NO_3)_3$ was Baker analysed reagent. Commercially available $KClO_3$ was recrystallized from hot water. All other chemicals used were of reagent grade.

Mixtures of $KClO_4$ and $Cr(NO_3)_3.9H_2O$, and $KClO_3$ and $Cr(NO_3)_3.9H_2O$ 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, taking care to see that absorption of moisture during the process is minimum.

The thermogravimetric studies were made in air using a Stanton recording thermobalance at a heating rate of 6°/min. About 100 mg samples were taken for each run in platinum crucibles. Differential thermal analyses were made on a Netzsch differential thermal analyser using standard alumina as reference material. About 70-100 mg samples were taken for each run and the heating rate of the furnace was adjusted to 10°/min. Constant temperature heating experiments were carried out using a muffle furnace, whose temperature could be controlled with an accuracy of ±10° in vitreosil crucible containers.

X-ray powder diffraction patterns were taken with a Philips X-ray generator using CuK_α radiation and a 11·46 cm diam Debye-Scherrer camera. Infrared spectra were recorded in the range 200-1400 cm^{-1} on a Beckman IR 12 spectrophotometer employing both KBr pellet and nujol mull techniques. Chromium(VI) and chloride contents are determined by the standard methods[3].

Results and Discussion

Thermal behaviour of 1:2, 1:1, 2:1, 4:1 *and* 8:1 *mixtures of* $KClO_4$ *and* $Cr(NO_3)_3.9H_2O$ — The thermogravimetric and DTA curves are given in Fig. 1. TG and DTA curves of 8:1 mixture are similar to those of 4:1. The curves indicate that the weight loss occurs at different temperature ranges. The first stage of decomposition sets in at 60° and is complete at 250°. The second stage commences around 310° and continues up to 360° and the final stage of decomposition occurs for the molar ratios greater than 1:1, in the temperature range 400-500°. Separate TG and DTA studies made on Cr(III) nitrate suggested that it melts around 70° and simultane usly dehydrates and decomposes to Cr_2O_3 at a single step in the temperature range 100-300°. The thermal behaviour of $KClO_4$ in the presence of Cr_2O_3 revealed[1] that Cr(III) is oxidized into $K_2Cr_2O_7$ in the temperature range 350-390° and the excess $KClO_4$ if any decomposed to KCl and oxygen above 400°.

The TG results of five different mixtures $KClO_4$ and $Cr(NO_3)_3.9H_2O$ given in Table 1, suggest that the first stage of weight loss is the decomposition of chromium(III) nitrate to Cr_2O_3, the second stage is its oxidation to $K_2Cr_2O_7$ and the final stage

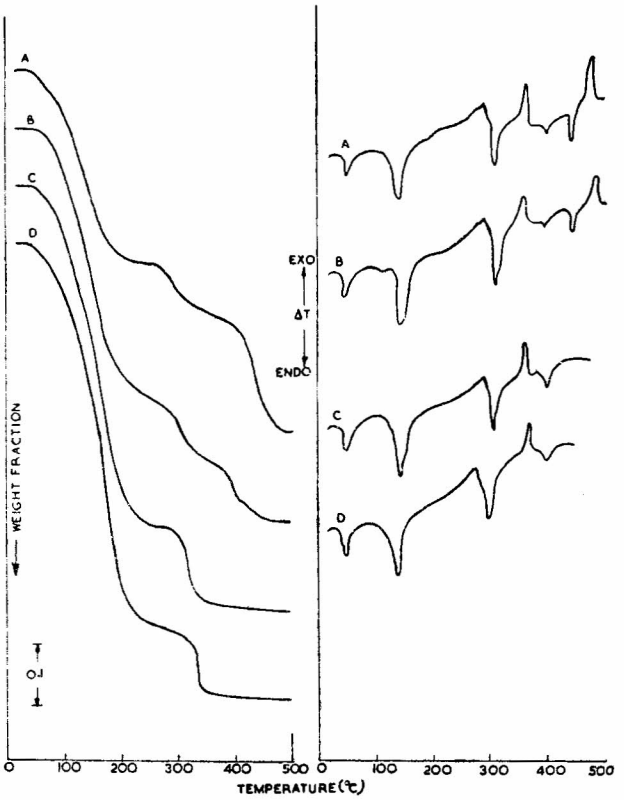

Fig. 1 — TG and DTA curves of 4:1 (A), 2:1 (B), 1:1 (C) and 1:2 (D) mixtures (molar ratios) of $KClO_4$ and $Cr(NO_3)_3.9H_2O$

is the decomposition of excess $KClO_4$. The different mixtures were heated to 480° in a muffle furnace and the products analysed by chemically X-ray and IR methods. Except for the residue of 1:2 mixture all the others were readily soluble in water, the insoluble part of the 1:2 mixture was found to be Cr_2O_3. The residues of 1:2 and 1:1 mixtures did not contain any chloride. The analytical values for the Cr(VI) and Cl^- content are given in Table 2.

The X-ray powder patterns of the residue of 1:1 mixture had d_{hkl} values (Å), 3·65m, 3·44m, 3·28s, 3·00s, 2·85s, 2·60w and 2·03w which are in good agreement[14] with those of $K_2Cr_2O_7$. The powder patterns of the residue of 1:2 mixture had d-spacings due to $K_2Cr_2O_7$ and additional lines (Å) at 3·63m, 2·68m, 2·49s and 1·67s which are characteristic[4] of Cr_2O_3. On the other hand, the X-ray patterns of the residues of 2:1, 4:1 and 8:1 molar ratios were identical and showed major lines of $K_2Cr_2O_7$ and extra lines (Å) at 3·16s, 2·20m and 1·82w, which agreed[4] with those of KCl.

The infrared spectra of the residues of 1:1, 2:1, 4:1 and 8:1 mixtures were identical and exhibited bands (cm^{-1}) at 1303w, 950s, b, 905s, 890s, 798s, 760s, 565m, 430w and 375m, characteristic[5,6] of $K_2Cr_2O_7$. The IR spectrum of the residue of 1:2 mixture showed bands corresponding to those of $K_2Cr_2O_7$ and additional bands at 620s, 555m and 400w characteristic of Cr_2O_3 (ref. 7).

The residues of the different mixture obtained by heating to 260° were found to be a mixture of $KClO_4$ and Cr_2O_3. The X-ray patterns indicated the lines due to Cr_2O_3 and extra lines at (Å) 3·54s, 3·15s and 2·88m characteristic of room temperature orthorhombic form of $KClO_4$ (ref. 4). The residues of molar ratios greater than 1:1 obtained by heating to 360° were identified to be the mixture of $K_2Cr_2O_7$ and $KClO_4$ by chemical, X-ray and infrared spectral analyses.

The results suggest that chromium(III) nitrate in the presence of $KClO_4$ decomposes to Cr_2O_3 in the temperature range 60-260° and the latter gets oxidized to $K_2Cr_2O_7$ between 310° and 360°. The unreacted $KClO_4$ in the molar ratios greater than 1:1 decomposes to KCl and oxygen in the temperature range 400-480°.

The endothermic DTA peaks observed at 60° and 160° for the mixtures are attributed to the melting and decomposition of chromium(III) nitrate respectively and that at 300° is due to the room temperature orthorhombic to cubic crystallographic phase transformation of $KClO_4$. The exotherm, peaking around 350° is

Table 2 — Analytical Data on the Residues of Decomposition of $KClO_4$ and $Cr(NO_3)_3.9H_2O$ Mixtures at 480°

Molar ratio [$KClO_4$: $Cr(NO_3)_3.9H_2O$]	Cr(VI) Found (%)	Extent of Cr(III) oxidation (%)	Chloride (%)	
			Found	Calc.
1:2	5·24	46·4	—	—
1:1	9·61	99·5	—	—
2:1	7·60	98·9	5·28	5·23
4:1	5·42	99·5	11·1	11·9
8:1	3·59	100·1	15·9	16·4

Table 1 — TG Data on the Decomposition of $KClO_4$ and $Cr(NO_3)_3.9H_2O$ Mixtures

Molar ratio [$KClO_4$: $Cr(NO_3)_3$ $9H_2O$]	Weight loss (%)					
	60-260°		310-360°		400-480°	
	Found	Calc.(a)	Found	Calc.	Found	Calc.(e)
1:2	70·0	69·0	77·0	76·0(b)	—	—
1:1	60·5	60·0	74·0	73·0(c)	—	—
2:1	47·0	47·0	57·5	58·0	69·0	68·0
4:1	34·0	34·0	41·5	41·0(d)	62·0	61·0
8:1	20·0	21·0	27·0	26·0	56·0	57·0

(a) $KClO_4 + Cr_2O_3$; (b) $K_2Cr_2O_7 + Cr_2O_3$; (c) $K_2Cr_2O_7$; (d) $K_2Cr_2O_7 + KClO_4$; (e) $K_2Cr_2O_7 + KCl$.

TABLE 3 — TG AND ANALYTICAL DATA ON THE DECOMPOSITION OF $KClO_3$ AND $Cr(NO_3)_3.9H_2O$ MIXTURES

Molar ratio [$KClO_3$: $Cr(NO_3)_3$ $9H_2O$]	Weight loss (%)		Cr(VI) found (%)	Extent of Cr(III) oxidation (%)	Chloride (%)	
	Found	Calc.			Found	Calc.
1:2	77·5	76·0	5·50	48·8	—	—
1:1	73·0	72·0	9·91	99·6	—	—
2:1	55·0	54·0	7·84	97·3	6·24	5·50
4:1	59·0	58·5	5·77	98·8	11·3	12·0
8:1	51·5	51·0	3·71	98·5	17·7	18·0

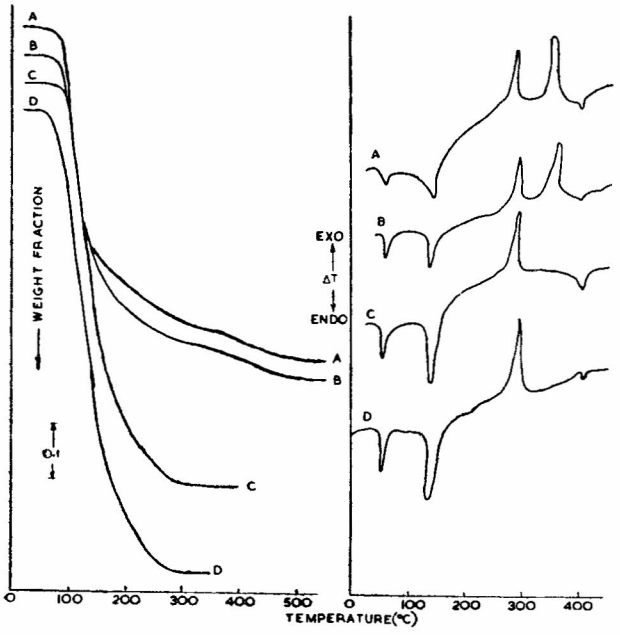

Fig. 2 — TG and DTA curves of 4:1 (A), 2:1 (B), 1:1 (C) and 1:2 mixtures (molar ratios) of $KClO_3$ and $Cr(NO_3)_3.9H_2O$

assigned to the oxidation of Cr(III) into $K_2Cr_2O_7$ and a small endotherm at 400° is due to the melting of $K_2Cr_2O_7$. An endotherm around 450° followed by an exotherm at 475° for the molar ratios greater than 1:1 is characteristic of $KClO_4$ decomposition[1].

Thermal behaviour of 1:2, 1:1, 2:1, 4:1 *and* 8:1 *mixtures of* $KClO_4$ *and* $Cr(NO_3)_3.9H_2O$ — The TG and DTA plots are given in Fig. 2. The curves for 8:1 mixture are similar to those of 4:1. The TG curves suggest that 2:1, 4:1 and 8:1 mixtures decomposed in two stages whereas 1:2 and 1:1 mixtures decomposed in a single step. The first stage of decomposition took place in the temperature range 100-300° and the second step occurred between 350° and 460°. The residues obtained by heating the mixtures to 460° were analysed and the analytical and the thermogravimetric results, given in Table 3, show that Cr(III) in 1:1 and higher molar ratios is completely oxidized to $K_2Cr_2O_7$. Further confirmation was provided by X-ray diffraction and IR spectral data. The residue of 1:1 mixture is found to be $K_2Cr_2O_7$ and that of 1:2 is a mixture of $K_2Cr_2O_7$ and Cr_2O_3. The decomposition products of mixtures in 2:1, 4:1 and 8:1 molar ratios are a mixture of $K_2Cr_2O_7$ and KCl. As in the case of $KClO_4$-$Cr(NO_3)_3.9H_2O$ system, chromium(III) nitrate in the presence of $KClO_3$ starts decomposing around 100° and gets oxidized to $K_2Cr_2O_7$ at 300° in a single step. The excess $KClO_3$ present in the 2:1, 4:1 and 8:1 molar ratios decomposes to KCl and oxygen in the temperature range 350-470°.

The DTA showed an endotherm at 60° due to the melting of chromium(III) nitrate and another endotherm around 140° due to its decomposition. An exotherm at 290° was attributed to the formation of $K_2Cr_2O_7$ and a small endotherm at 400° was due to the melting of $K_2Cr_2O_7$. The mixtures in 2:1, 4:1 and 8:1 molar ratios showed an exotherm around 350° assigned[2] to the decomposition of $KClO_3$. It is interesting to note that when $KClO_3$ is heated in the presence of Cr_2O_3, each g-ion of Cr(III) takes up 4·3 moles of $KClO_3$ to get oxidized[2] whereas in the presence of chromium(III) nitrate, one mole of $KClO_3$ is sufficient to oxidize a g-ion of Cr(III). This is probably due to the fact that oxygen liberated during the decomposition of nitrate moiety at this temperature is also used up in the oxidation of Cr(III).

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