

Note

Thermogravimetric analysis of some higher carboxylate derivatives of chromium(III)

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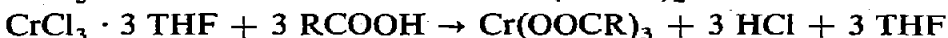
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A number of chromium carboxylates have been synthesised in these laboratories¹ and their physico-chemical and structural properties have been investigated in detail. Under the present communication, the results of thermogravimetric analysis of some of these derivatives are reported.

EXPERIMENTAL

Carboxylate derivatives of chromium(III) have been synthesised by the reaction of $\text{CrCl}_3 \cdot \text{THF}$ with various fatty acids in different stoichiometric ratios:



where $\text{R} = \text{C}_{11}\text{H}_{23}$, $\text{C}_{15}\text{H}_{31}$, $\text{C}_{17}\text{H}_{35}$ and $\text{C}_{21}\text{H}_{43}$.

The chloride derivatives are viscous liquids and sensitive to moisture, whereas tris-derivatives are solid, highly stable and have been purified by repeated crystallisation from anhydrous benzene. The purity of these derivatives is established by elemental analysis and spectroscopic methods.

Thermogravimetric analysis of these compounds is carried out by an automatic recording Stanton thermobalance. Pre-weighed samples in platinum crucibles are heated in the furnace of the balance in contact with air and the effect of temperature on the mass of these derivatives is recorded on a chart paper of a dual pen recorder. The heated samples are taken out at specific stages and analysed in order to establish the mode of decomposition. Thermal decomposition curves showing loss in weight at various temperatures and corresponding differential thermal graphs (DTG, weight loss per 5 min vs. temperature) are plotted in Figs. 1-4. The summary of the results depicting temperatures at which significant changes are noticed, along with observed/calculated yield of chromium oxide in each case are summarised in Table 1.

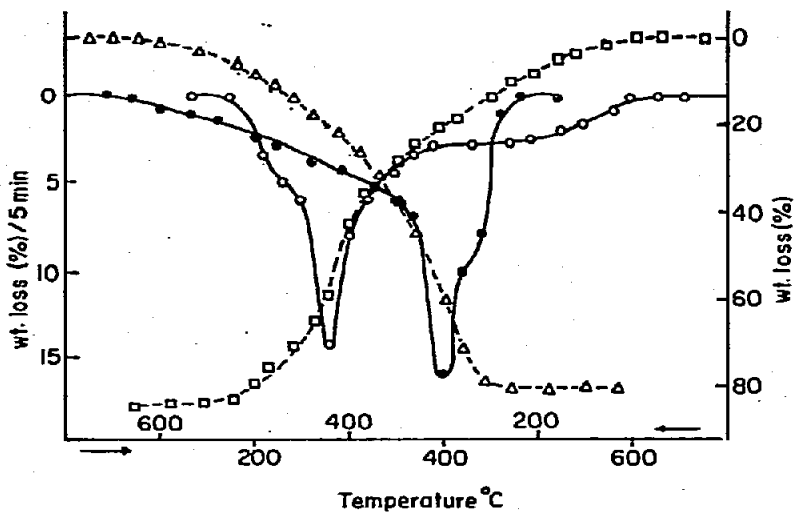


Fig. 1. ●, ▲, $\text{CrCl}_2(\text{OOCC}_{11}\text{H}_{23}) \cdot \text{THF}$; ○, □, $\text{CrCl}_2(\text{OOCC}_{15}\text{H}_{31}) \cdot \text{THF}$.

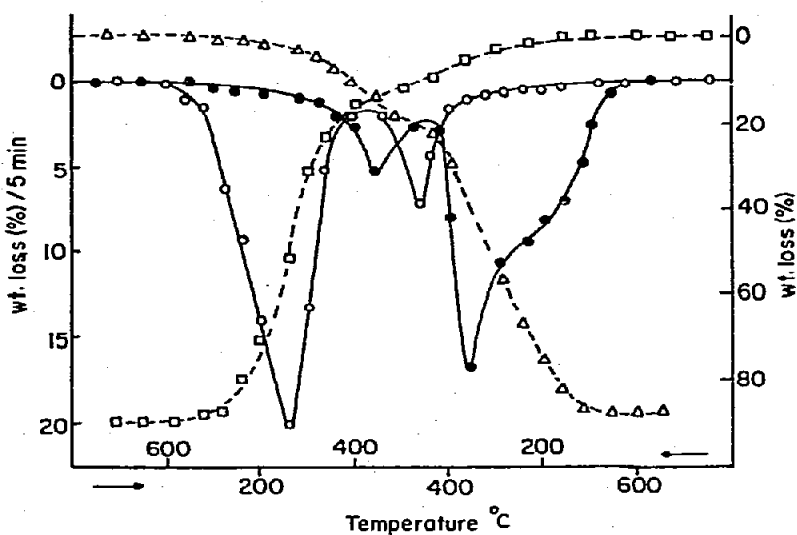


Fig. 2. ●, ▲, $\text{CrCl}(\text{OOCC}_{15}\text{H}_{31})_2$; ○, □, $\text{CrCl}(\text{OOCC}_{21}\text{H}_{43})_2$.

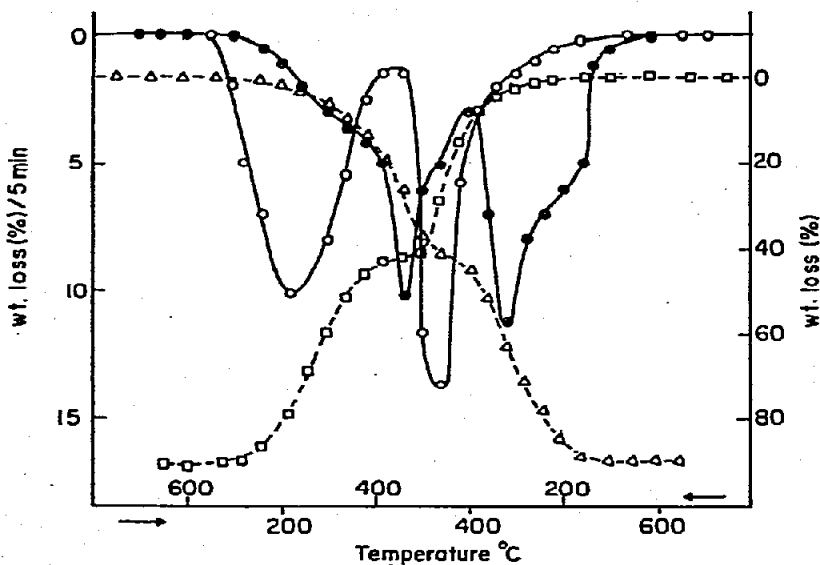


Fig. 3. ●, ▲, $\text{Cr}(\text{OOCC}_{11}\text{H}_{23})_3$; ○, □, $\text{Cr}(\text{OOCC}_{15}\text{H}_{31})_3$.

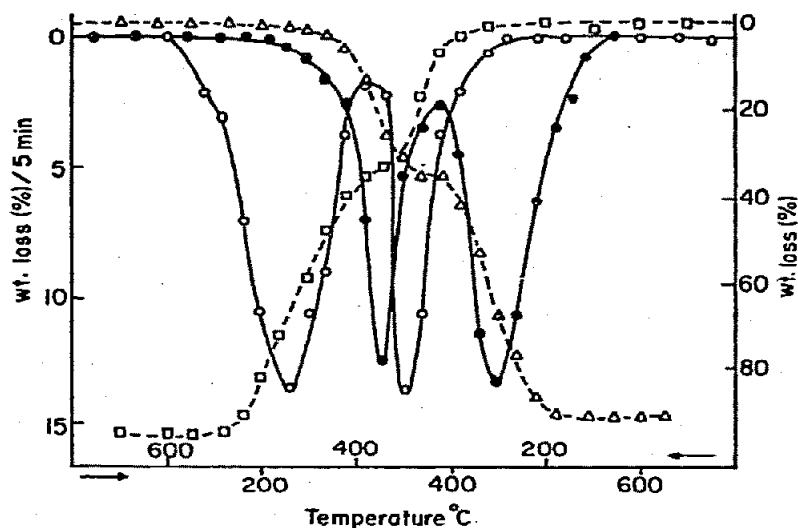


Fig. 4. ●, △, $\text{Cr}(\text{OOCC}_{17}\text{H}_{35})_3$; ○, □, $\text{Cr}(\text{OOCC}_{21}\text{H}_{43})_3$.

TABLE I

THERMOGRAVIMETRIC ANALYSIS OF CHROMIUM (III) CARBOXYLATES

Compound	Decomposition temperature ($^{\circ}\text{C}$)			Metal oxide (%) (Calc.)
	Initial ^a	Maximum ^b	Final ^c	
$\text{CrCl}_2(\text{OOCC}_{11}\text{H}_{23}) \cdot \text{THF}$	100	400	480	19.20 (19.29)
$\text{CrCl}_2(\text{OOCC}_{15}\text{H}_{31}) \cdot \text{THF}$	120	420	520	16.95 (16.88)
$\text{CrCl}_2(\text{OOCC}_{17}\text{H}_{35}) \cdot \text{THF}$	120	440	540	10.10 (15.90)
$\text{CrCl}(\text{OOCC}_{11}\text{H}_{23})_2$	140	310 440	560	15.82 (15.66)
$\text{CrCl}(\text{OOCC}_{15}\text{H}_{31})_2$	160	320 450	580	12.90 (12.71)
$\text{CrCl}(\text{OOCC}_{21}\text{H}_{43})_2$	180	320 470	600	10.04 (9.93)
$\text{Cr}(\text{OOCC}_{11}\text{H}_{23})_3$	180	330 440	540	11.40 (11.71)
$\text{Cr}(\text{OOCC}_{15}\text{H}_{31})_3$	210	340 480	560	9.35 (9.29)
$\text{Cr}(\text{OOCC}_{17}\text{H}_{35})_3$	230	330 450	560	8.33 (8.44)
$\text{Cr}(\text{OOCC}_{21}\text{H}_{43})_3$	250	350 480	580	7.02 (7.11)

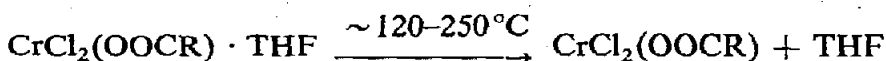
^a Temperature at which decomposition starts.

^b Temperature at which maximum decomposition is observed.

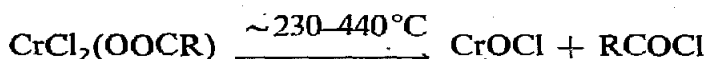
^c Temperature at which the decomposition is complete, with the formation of chromium tri-oxide as final product.

RESULTS AND DISCUSSION

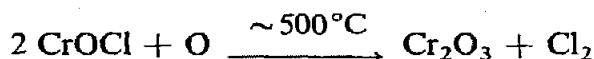
Chromium dichloride monocarboxylate monotetrahydrofuran adducts, $\text{CrCl}_2(\text{OOCR}) \cdot \text{THF}$, where $\text{R} = \text{C}_{11}\text{H}_{23}$, $\text{C}_{15}\text{H}_{31}$ and $\text{C}_{17}\text{H}_{35}$, are found to be thermally stable up to 120°C . A slow decomposition starts after $\sim 120^\circ\text{C}$ and continues up to $\sim 250^\circ\text{C}$. The loss in weight corresponds to the liberation of 1 mole of tetrahydrofuran (THF).



The decomposition of chromium dichloride monocarboxylate, $\text{CrCl}_2(\text{OOCR})$, begins around $\sim 240^\circ\text{C}$ and becomes rapid around 400°C , as evident from corresponding DTG and TGA curves (Fig. 1). The product left in the crucible in the range $\sim 420-440^\circ\text{C}$ corresponds mainly in weight and analysis to chromium oxychloride.

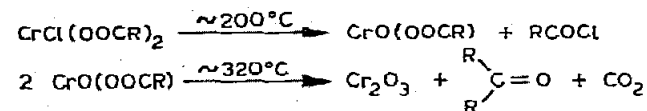


Chromium oxychloride also starts decomposing above 400°C and is converted to chromic oxide near 500°C .



The depression in DTG curves near 400°C is due to the decomposition of the RCOCl form in the course of thermal decomposition of the product. The final product left in the crucible corresponds mainly to chromic oxide but the formation of traces of higher and lower oxides along with tri-oxide cannot be ruled out.

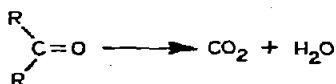
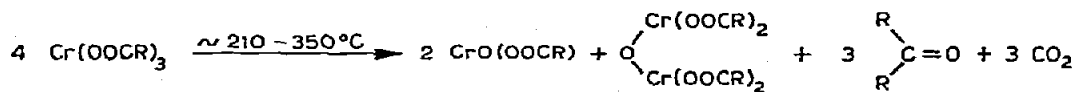
Chromium monochloride dicarboxylates, $\text{CrCl}(\text{OOCR})_2$, follow a different route of decomposition. The TGA and DTG curves (Fig. 2) show that these derivatives are quite stable up to $\sim 180^\circ\text{C}$. These derivatives undergo slow decomposition above $\sim 180^\circ\text{C}$ with the appearance of two distinct depressions in their DTG curves at ~ 320 and $\sim 470^\circ\text{C}$. The first depression may be due to the liberation of CO_2 formed during the decomposition



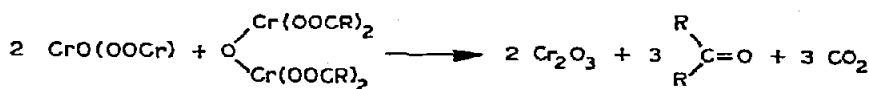
Corresponding acyl halides and ketones undergo rapid decomposition at about $\sim 480^\circ\text{C}$. The formation of ketone in the decomposition of higher carboxylate derivatives of cobalt², aluminium³ and lanthanides⁴ has also been observed in earlier studies.

The mode of decomposition of chromium tricarboxylates, $\text{Cr}(\text{OOCR})_3$, is found to be different to that of aluminium tricarboxylates³. The appearance of two equally strong depressions in the DTG curves (Figs. 3 and 4) indicate a two-step decomposition. These derivatives remain stable up to 210°C and then a slow de-

composition starts with the liberation of carbon dioxide. The corresponding ketones formed in the process also undergo decomposition. Chromium oxycarboxylates formed in the decomposition process remain stable up to $\sim 350^\circ\text{C}$. The first mode of decomposition may be represented as



Chromium oxycarboxylates undergo further decomposition above 380°C with the formation of chromium trioxide and the corresponding ketones. These ketones rapidly undergo decomposition at such high temperature in the presence of air



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