

Thermal decomposition of analytically important thiocyanatochromates(III).

Part 2

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Abstract

The thermal decomposition of the crystalline complex salts $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ and $\text{Bi}[\text{Cr}(\text{SCN})_6]$ has been studied. On the basis of the thermal analysis, and from the X-ray diffraction and chemical analyses of their decomposition products, schematic representations of their thermal decomposition reactions have been established. From their thermogravimetric curves, the activation energies and reaction orders have been calculated. A comparison of the thermal stability of the compounds is made.

INTRODUCTION

The present work is a continuation of our studies on the thermal decomposition of crystalline hexathiocyanatochromates(III). The previous paper [1] discussed the thermal decomposition reactions of $\text{Ag}_3[\text{Cr}(\text{SCN})_6]$, $\text{Tl}_3[\text{Cr}(\text{SCN})_6]$ and $\text{Hg}_3[\text{Cr}(\text{SCN})_6]_2$. The kinetic parameters were calculated from their thermogravimetric curves. A comparison of the thermal stability of these compounds was made.

The subject of the present work is the study of the thermal decomposition in dynamic conditions and the evaluation of the kinetic parameters of the decomposition reactions of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ and $\text{Bi}[\text{Cr}(\text{SCN})_6]$.

The sparingly soluble bismuth hexathiocyanatochromate prepared by Mahr [2] has been used for the gravimetric determination of bismuth [3]. Roesler described the preparation of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ [4]. Cherkasova stated that the solid decomposition products of lead and bismuth hexathiocyanatochromates heated at 700°C are $\text{Cr}_2\text{O}_3 + \text{Pb}_3\text{O}_4$ or $\text{Cr}_2\text{O}_3 + \text{Bi}_2\text{O}_3$, respectively [5].

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EXPERIMENTAL

Apparatus

The apparatus and measuring conditions were the same as described in our previous paper [1].

Preparation, chemical and X-ray analyses

Lead hexathiocyanatochromate(III) was prepared by adding excess $K_3[Cr(SCN)_6]$ crystals to a solution of 3 g $Pb(NO_3)_2$ in 100 ml of water. Fine yellow crystals of $Pb_3[Cr(SCN)_6]_2$ were immediately formed. They were filtered off using a G-4 sintered glass crucible, rinsed with water and dried in air at ambient temperature. Bismuth hexathiocyanatochromate(III) was prepared as follows: to 1 g of $K_3[Cr(SCN)_6]$ dissolved in 25 ml of water were added 3–4 g of activated charcoal; after mixing it was filtered off. The filtrate was dropped into a solution of 190 mg $Bi(NO_3)_3$ in 1 M HNO_3 heated at 30°C. After several seconds, fine, dark-red crystals of $Bi[Cr(SCN)_6]$ were formed. They were filtered off, rinsed with cold water and dried in air at 120–130°C. $K_3[Cr(SCN)_6]$ was obtained by the method described in the literature [6].

The chemical composition of the compounds under study was confirmed by chemical analysis. Lead was determined by complexometric titration with EDTA using pyrogallol red as indicator; bismuth was determined gravimetrically as Bi_2S_3 , and thiocyanate was determined using the method described by Mueller [3]. The solubility in water of the lead and bismuth hexathiocyanatochromates(III) was also determined. The chemical analyses and solubility results are presented in Table 1.

TABLE 1

Results of chemical analysis and solubility in water of lead and bismuth hexathiocyanatochromates(III)

Colour of precipitate	Outer sphere cation/%	SCN^- /%	Solubility/($g\ l^{-1}$)
$Pb_3[Cr(SCN)_6]_2$ Yellow-orange	43.41	47.50	2.51×10^{-3}
$Bi[Cr(SCN)_6]$ Dark red	34.62	55.50	0.02×10^{-3}

TABLE 2

X-ray diffraction data of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ and $\text{Bi}[\text{Cr}(\text{SCN})_6]$

$\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$		$\text{Bi}[\text{Cr}(\text{SCN})_6]$	
<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>
7.90	27.0	6.92	46.4
5.34	25.0	6.03	76.8
4.98	58.0	5.95	100.0
4.48	88.0	4.19	84.8
4.11	100.0	3.99	7.3
3.02	18.0	3.59	9.1
2.96	15.0	3.43	23.2
2.84	22.0	3.33	5.5
2.81	58.0	3.17	3.6
2.75	87.0	2.73	33.0
2.62	26.0	2.68	30.3
2.58	24.0	2.44	21.4
2.31	32.0	2.42	12.5
2.26	30.0	2.28	5.5
2.21	25.0	2.12	13.4
1.93	19.0	1.90	9.8
1.90	23.0	1.88	6.4
1.74	9.0		
1.68	15.0		
1.54	11.0		
1.42	13.0		

$\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ and $\text{Bi}[\text{Cr}(\text{SCN})_6]$ exhibit well-defined diffraction patterns with a large number of sharp peaks, confirming that these compounds are crystalline. X-ray diffraction data are listed in Table 2.

Thermoanalytical studies

The thermal analysis curves of the compounds under study are shown in Figs. 1 and 2. The slight decrease in mass ($\approx 3\%$) observed on the TG curve of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ (Fig. 1) within the temperature range 160–250°C is connected with the removal of hygroscopic water and volatile surface impurities from the sample. The corresponding small, sharp peak on the DTG curve is at 240°C. The main stage of the decomposition of lead hexathiocyanatochromate(III) takes place between 270 and 440°C, with the mass loss determined from the TG curve being 22%. The corresponding large, exothermic peak on the DTA curve begins at 280°C, has two indistinct overlapping maxima and finishes at 500°C. A slight increase in

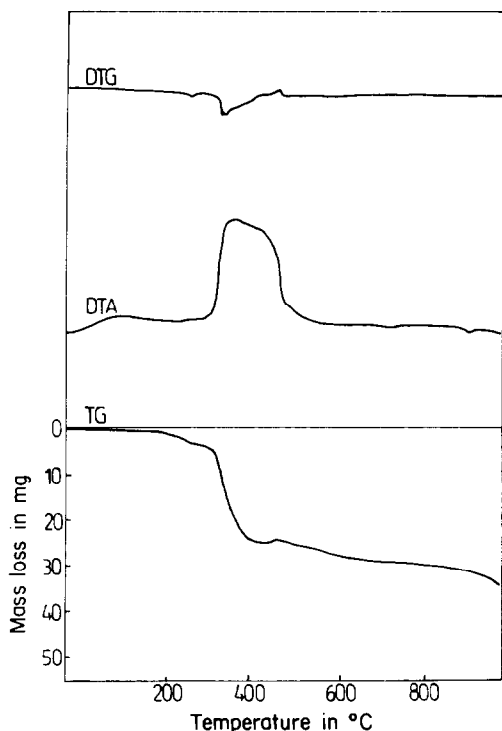


Fig. 1. Thermal analysis curves of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$.

mass visible on the TG curve at about 460°C is followed by a continuous slow mass loss. The small, sharp endothermic DTA peak at 900°C probably corresponds to the gradual, slow thermal decomposition of PbSO_4 . At 1000°C , the total loss of mass is about 38%.

The thermoanalytical curves of bismuth hexathiocyanatochromate(III) (Fig. 2) are similar to those of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$. After a slight loss of mass ($\approx 2\%$) at low temperatures ($180\text{--}220^\circ\text{C}$), the main stage of the decomposition reaction takes place within the range $280\text{--}520^\circ\text{C}$, the loss of mass determined from the TG curve being 35%. The corresponding exothermic peak on the DTA curve is high and broad ($300\text{--}500^\circ\text{C}$) and is probably composed of two overlapping exothermic effects. The second decomposition step of the bismuth salt visible on the TG curve takes place within the temperature range $500\text{--}740^\circ\text{C}$ and is accompanied by a mass loss of about 7%. The corresponding DTA peak is barely registered at 620°C . At 960°C , the complete loss in mass is 47%.

In order to follow the course of the thermal decomposition of the hexathiocyanatochromates under study, 100 mg samples of these compounds were heated in a silite furnace in conditions similar to those under which the thermal curves were obtained up to the temperatures determined from the TG curves corresponding to the end of each particular stage of the

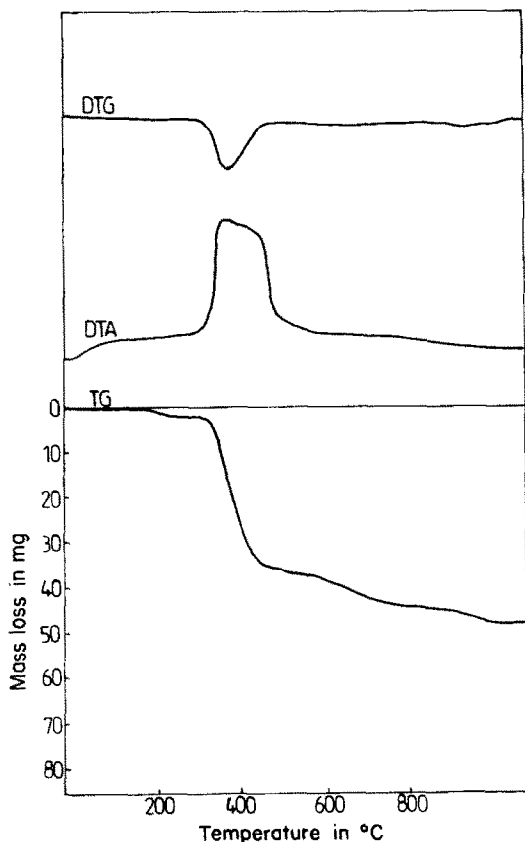


Fig. 2. Thermal analysis curves of $\text{Bi}[\text{Cr}(\text{SCN})_6]$.

reaction. Sinters of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ were prepared at 295, 395 and 660°C and of $\text{Bi}[\text{Cr}(\text{SCN})_6]$ at 260, 650 and 920°C.

The diffraction pattern of the lead salt heated at 295°C is similar to that of the original compound but the corresponding peaks are lower and more diffuse (Fig. 3). The sinter obtained at 395°C exhibits an entirely different diffraction pattern. The few low, diffuse peaks suggest a low degree of crystallinity of the sinter. The diffraction pattern of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ heated at 660°C is almost identical to that of PbSO_4 .

The diffraction pattern of $\text{Bi}[\text{Cr}(\text{SCN})_6]$ heated at 260°C is the same as that of the original compound (Fig. 4). The sinter obtained at 650°C is amorphous. The diffraction pattern of the sinter prepared at 920°C indicates the presence of $(\text{BiO})_2\text{SO}_4$ in the final solid decomposition products of bismuth hexathiocyanatochromate(III). There are no peaks characteristic of Cr_2O_3 .

The kinetic parameters (activation energy and reaction order) of the main stages of the thermal decomposition reactions of the compounds under study were determined from the thermogravimetric curves using the

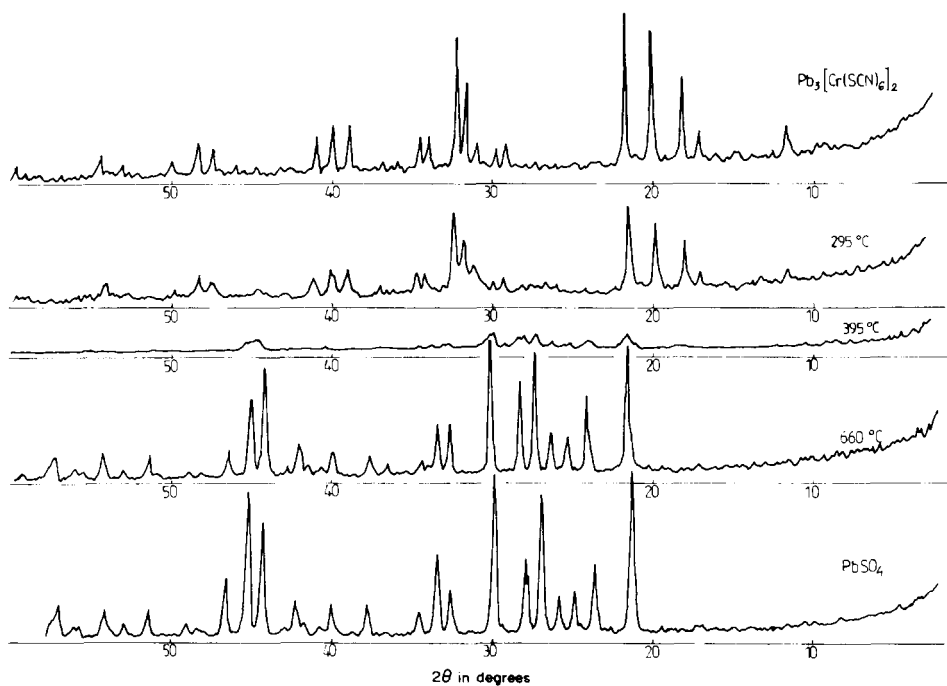


Fig. 3. X-ray diffraction patterns of $Pb_3[Cr(SCN)_6]_2$, sinters and $PbSO_4$.

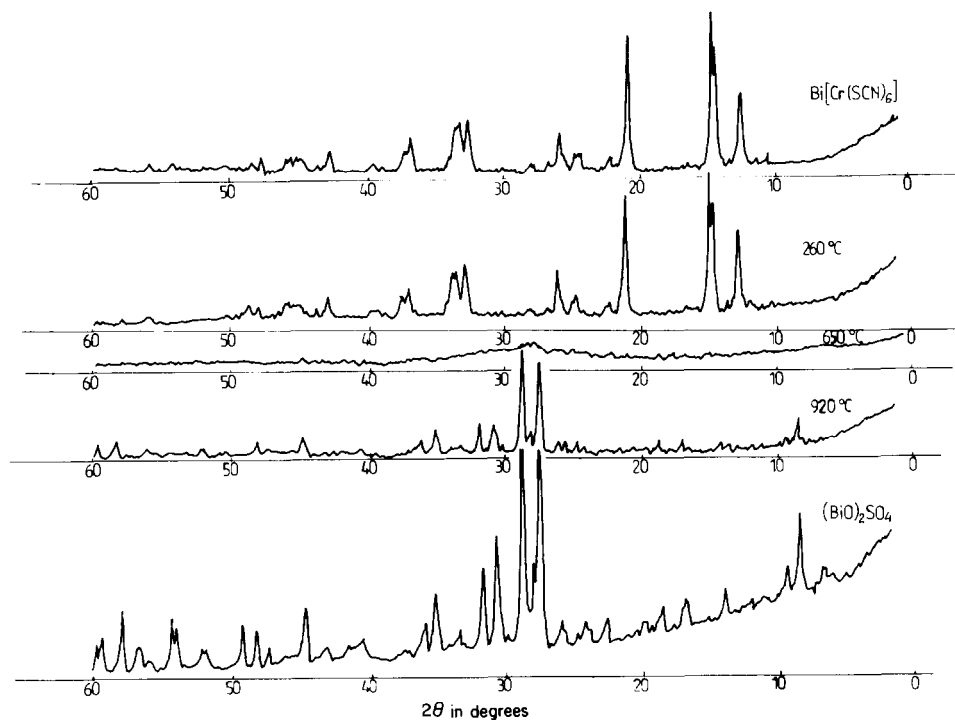


Fig. 4. X-ray diffraction pattern of $Bi[Cr(SCN)_6]$, sinters and $(BiO)_2SO_4$.

TABLE 3

Kinetic parameters of the thermal decomposition reactions of lead and bismuth hexathiocyanatochromates(III)

Coats–Redfern method		Zsako method	
$E/(\text{kJ mol}^{-1})$	n	$E/(\text{kJ mol}^{-1})$	n
$\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ 133.0	1.9	134.0	1.9
$\text{Bi}[\text{Cr}(\text{SCN})_6]$ 186.4	1.7	184.2	1.7

Coats and Redfern [7] and Zsako [8] methods. The final results are listed in Table 3.

CONCLUSIONS

The lead and bismuth hexathiocyanatochromates(III) of formulae $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ and $\text{Bi}[\text{Cr}(\text{SCN})_6]$, as determined by the chemical analyses, separate instantly from the mother solutions at room temperature in the form of fine, well-formed crystals of characteristic colour. The X-ray diffraction patterns indicate that these complexes have well-defined structures. They are sparingly soluble in water, particularly the bismuth salt (Table 1). Their solubility, as compared with the solubilities of the compounds investigated earlier [1] increases in the order: $\text{Bi}[\text{Cr}(\text{SCN})_6] \ll \text{Ag}_3[\text{Cr}(\text{SCN})_6] < \text{Hg}_3[\text{Cr}(\text{SCN})_6]_2 \approx \text{Ti}_3[\text{Cr}(\text{SCN})_6] \ll \text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$.

The thermal decomposition of the lead and bismuth salts takes place within the ranges 170–390°C and 260–520°C, respectively, and is not preceded by the melting of the samples. According to the chemical and X-ray analyses of the solid intermediate and final products of decomposition of $\text{Bi}[\text{Cr}(\text{SCN})_6]$, amorphous Cr_2O_3 and crystalline $(\text{BiO})_2\text{SO}_4$, with an admixture of Bi_2O_3 , are formed (Fig. 4). The final solid products of decomposition of $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$ are crystalline PbSO_4 and amorphous Cr_2O_3 (Fig. 3). This is not consistent with the conclusions of other authors [5]. The gaseous pyrolysis products of both compounds are probably CO_2 , SO_2 and N_2 (qualitative statement). The following summary schemes for the thermal decomposition of the compounds under study can be proposed



The thermal stabilities of lead and bismuth hexathiocyanatochromates

and of those studied earlier [1], as defined by the temperature at which the decomposition starts, increase in the order: $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2 < \text{Hg}_3[\text{Cr}(\text{SCN})_6]_2 < \text{Ag}_3[\text{Cr}(\text{SCN})_6] < \text{Bi}[\text{Cr}(\text{SCN})_6] < \text{Tl}_3[\text{Cr}(\text{SCN})_6]$.

Taking into account the low solubility in water of the compounds under study, bismuth and lead can be determined quantitatively in water solutions as $\text{Bi}[\text{Cr}(\text{SCN})_6]$ and $\text{Pb}_3[\text{Cr}(\text{SCN})_6]_2$. The precipitates should be dried in air below 250°C for the bismuth salt, and below 160°C for the lead salt.

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