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Thermal decomposition of analytically important thiocyanatochromates(III).
Part 1

Bogdan Ptaszyński * and Elżbieta Skiba

Institute of General and Ecological Chemistry, Polytechnical University, 90924 Łódź (Poland)

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Abstract

Thermoanalytical studies carried out on complex salts $Ag_3[Cr(SCN)_6]$, $Tl_3[Cr(SCN)_6]$ and $Hg_3[Cr(SCN)_6]_2$. On the basis of thermal analysis, and X-ray and chemical analyses of their decomposition products, schematic representations of the thermal decomposition reactions were established. From thermogravimetric curves, kinetic parameters were calculated using the methods of Coats–Redfern and Zsako. A comparison of the thermal stabilities of the compounds was made.

INTRODUCTION

Hexathiocyanatochromate(III) compounds form a large group of complex salts known since Roesler reported the preparation of $(NH_4)_3$-$[Cr(SCN)_6]$, $K_3(Cr(SCN)_6]$, $Ag[Cr(SCN)_6]$ and $Pb_3[Cr(SCN)_6$ [1]. Mohr obtained $Bi[Cr(SCN)_6]$ [2] and Karantasis and Sakellaridis succeeded in synthesizing $Hg_3[Cr(SCN)_6]_2$ and $Tl[Cr(SCN)_6]$ [3]. Some thiocyanatochromate(III) compounds have found analytical application, e.g. the very sparingly soluble bismuth heathiocyanatochromate has been used for the gravimetric determination of bismuth. The subject of the present work is a study of the thermal decomposition in dynamic conditions and an evaluation of the kinetic parameters of the decomposition reactions, for $Ag_3[Cr(SCN)_6]$, $Tl_3[Cr(SCN)_6]$ and $Hg_3[Cr(SCN)_6]_2$. Precise thermoanalytical studies of these compounds have not previously been performed. On the DTA curve of $Tl_3[Cr(SCN)_6]$ Cherkasova et al. have found curve of $Tl_3[Cr(SCN)_6]$ overlapping exothermic effects within a temperature range of 300–500°C [4]. These authors have also published the thermoanalytical curves of $Ag_3[Cr(SCN)_6]$ and stated that the solid decomposition product of this compound is a mixture of Cr_2O_3 and $Ag_2Cr_2O_7$ [5]. According to Liptay

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* Corresponding author.

et al. the final solid products of the thermal decomposition of thallium(I), silver(I) and potassium hexathiocyanatochromates correspond to a stoichiometric mixture of $Cr_2O_3 + M_2SO_4$ [6].

EXPERIMENTAL

Apparatus

Thermal analysis of the compounds under study was carried out using a derivatograph MOM Budapest type OD-102/1500°C.

The measurements were made in air over the temperature range 20–1000°C at a heating rate of 5°C min^{-1}. DTA and DTG sensitivities were both 1/10 and the TG sensitivity was 100 mg. The mass of the sample was 100 mg. α-Al_2O_3 was used as a reference material.

In order to follow the course of the thermal decomposition samples of about 100 mg were heated in VEB Electro-Industrieofenbau Römbild type KO14 furnace at a rate of 5°C min^{-1} to the appropriate temperature determined from the thermal analysis curves.

The X-ray diffraction patterns of the original compounds and the sinters were obtained using a DRON-1 diffractometer with a nickel-filtered Cu Kα radiation source. The intensity of the reflections was measured with a scintillation counter SRS I-0. Diffracted rays were recorded with an automatic recorder over the range of 2θ angles 2–60°.

Preparation, chemical and X-ray analyses

Silver and thallium hexathiocyanatochromates were prepared by dissolving the appropriate quantity of $AgNO_3$ or $TlNO_3$ in 0.1 M HNO_3 and slowly adding an excessive of 5% $K_3[Cr(SCN)_6]$ solution. Fine precipitates of $Ag_3[Cr(SCN)_6]$ (pink) and $Tl_3[Cr(SCN)_6]$ (grey) were immediately formed. They were heated on the water bath for about 1 h, filtered off and dried in air ambient temperature. A brown precipitate of $Hg_3[Cr(SCN)_6]_2$ was prepared analogously, using $HgCl_2$ solution in dilute hydrochloric acid. $K_3[Cr(SCN)_6]$ was obtained by the method described in the literature [1].

The chemical compositions of the compounds under study were confirmed by chemical analysis. Thiocyante was determined by the method described by Mueller [7]; the outer sphere metals were determined gravimetrically as AgCl, TlI and HgS. The solubilities of the compounds in water at room temperature were also determined. The results of the analyses and the solubility determinations of the compounds under study are presented in Table 1.

$Ag_3[Cr(SCN)_6]$ and $Tl_3[Cr(SCN)_6]$ exhibit well-defined diffraction patterns revealing the structures of these compounds to be crystalline, whereas the diffraction pattern of $Hg_3[Cr(SCN)_6]_2$ indicates that this salt is

TABLE 1

Results of chemical analysis and solubility in water of hexathiocyanatochromate(III) salts

Compound	Colour of precipitate	Outer sphere cation (wt.%)	SCN^- (wt.%)	Solubility ($g\,l^{-1}$)
$Ag_3[Cr(SCN)_6]$	Pink	44.72	47.60	0.6×10^{-3}
$Tl_3[Cr(SCN)_6]$	Grey	60.51	60.36	1.7×10^{-3}
$Hg_3[Cr(SCN)_6]_2$	Brown	41.30	48.98	1.6×10^{-3}

TABLE 2

X-Ray diffraction data of silver and thallium hexacyanatochromate(III) salts

$Ag_3[Cr(SCN)_6]$		$Tl_3[Cr(SCN)_6]$	
d/n	*I*	*d/n*	*I*
7.14	53.1	7.10	72.7
7.02	46.9	7.08	48.5
4.15	100.0	6.86	36.4
3.60	40.6	4.70	93.9
2.73	50.0	4.40	36.4
2.72	40.6	4.25	36.4
2.53	21.9	4.00	42.4
2.41	25.0	3.13	66.7
2.21	18.7	3.06	100.0
2.02	25.0	2.99	45.4
2.75	40.6	2.86	42.4
2.53	25.0	2.76	15.1
		2.36	15.1
		2.23	18.2
		2.13	12.1

amorphous. X-ray diffraction data of silver and thallium hexathiocyanatochromates are presented in Table 2.

Thermoanalytical studies

Thermal analysis curves of the compounds under study are shown in Figs. 1–3. The slight decrease in mass (2–3%) at low temperatures are connected with the removal of hygroscopic water and volatile impurities of the samples. On the DTA curves no peaks corresponding to the melting of the compounds are observed. The TG and DTG curves of $Ag_3[Cr(SCN)_6]$ (Fig. 1) show two gradual overlapping stages of decomposition with a loss of mass of 28% within the temperature range 230–440°C. The DTA curve shows a large exothermic peak beginning at 320°C with two weak maxima

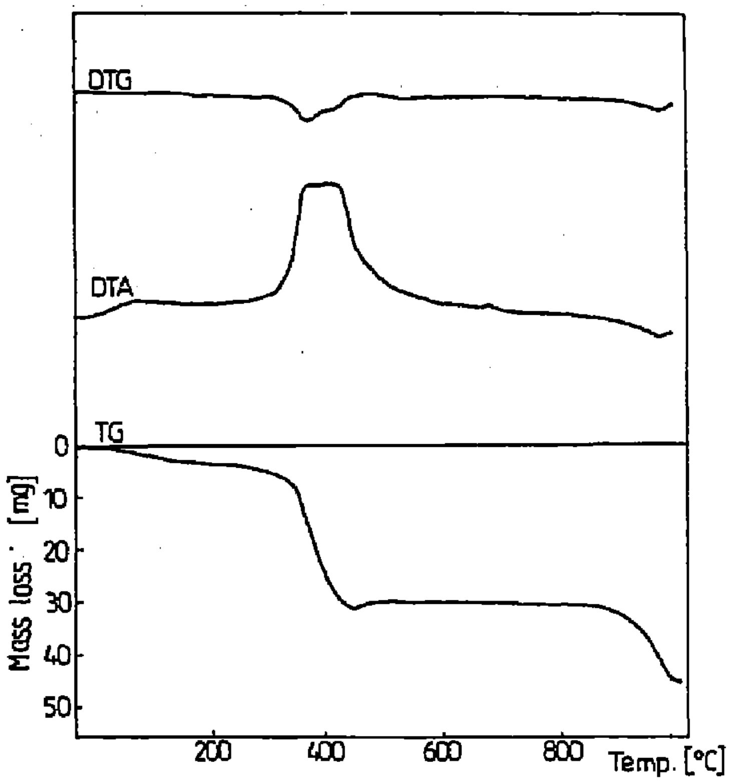

Fig. 1. Thermal analysis curves of $Ag_3[Cr(SCN)_6]$.

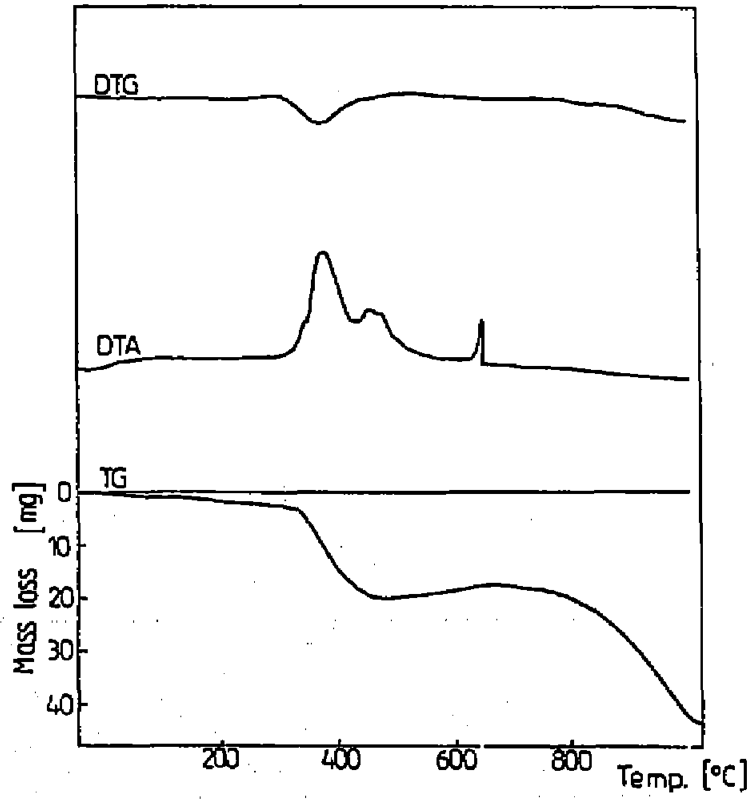

Fig. 2. Thermal analysis curves of $Tl_3[Cr(SCN)_6]$.

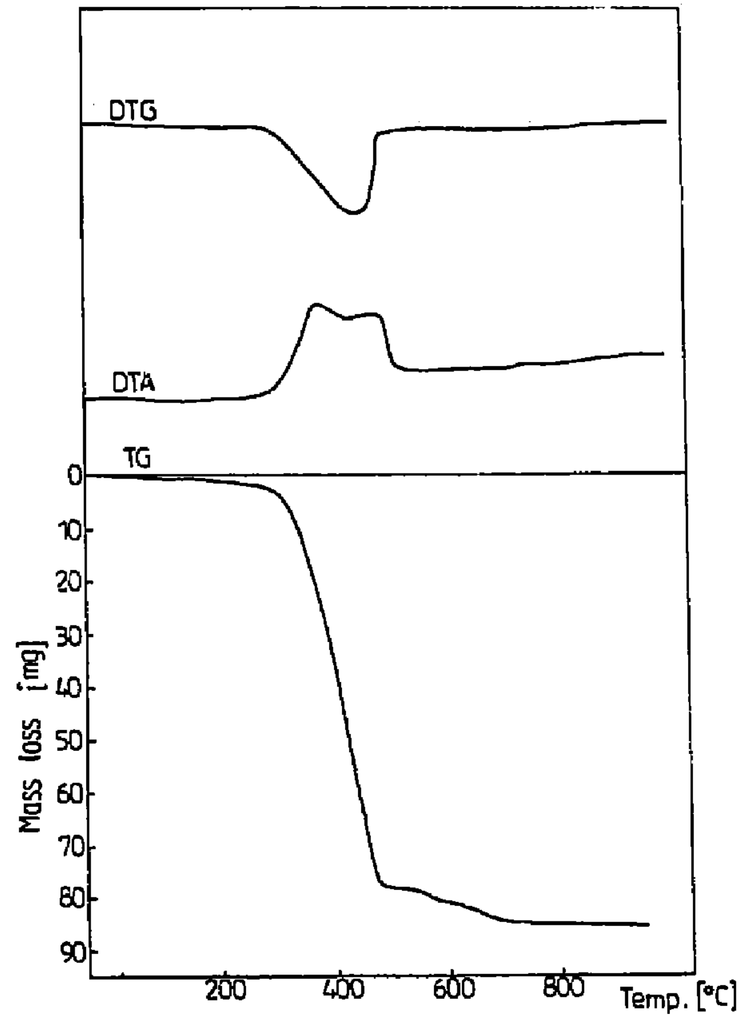

Fig. 3. Thermal analysis curves of $Hg_3[Cr(SCN)_6]_2$.

at 360°C and 420°C and finishing at 560°C. The small but distinct peak at 660°C corresponds to the melting of one of the solid decomposition products (Ag_2SO_4). At high temperatures on the DTA curve a small sharp endothermic peak at 980°C is observed. This corresponds to the fast loss of mass connected with the evaporation of the molten Ag_2SO_4.

The thermoanalytical curves of $Tl_3[Cr(SCN)_6]$ are shown in Fig. 2. A loss of mass of 17% takes place within the temperature range 320–460°C and is accompanied by a large exothermic effect with two peaks: high at 450°C; distinctly lower at 470°C. The slight increase in mass of about 3% observed on the TG curve is probably a result of oxidation of the decomposition product of the original compound to thallium sulphate. A corresponding sharp exothermic peak occurs at 630°C.

The main step in the thermal decomposition of $Hg_3[Cr(SCN)_6]_2$ (Fig. 3) takes place within the temperature range 220–470°C. The appropriate loss of mass (77%) is related to the occurrence of a broad exothermic peak with two maxima: 370 and 480°C. Above 470°C a slow mass decrease of about

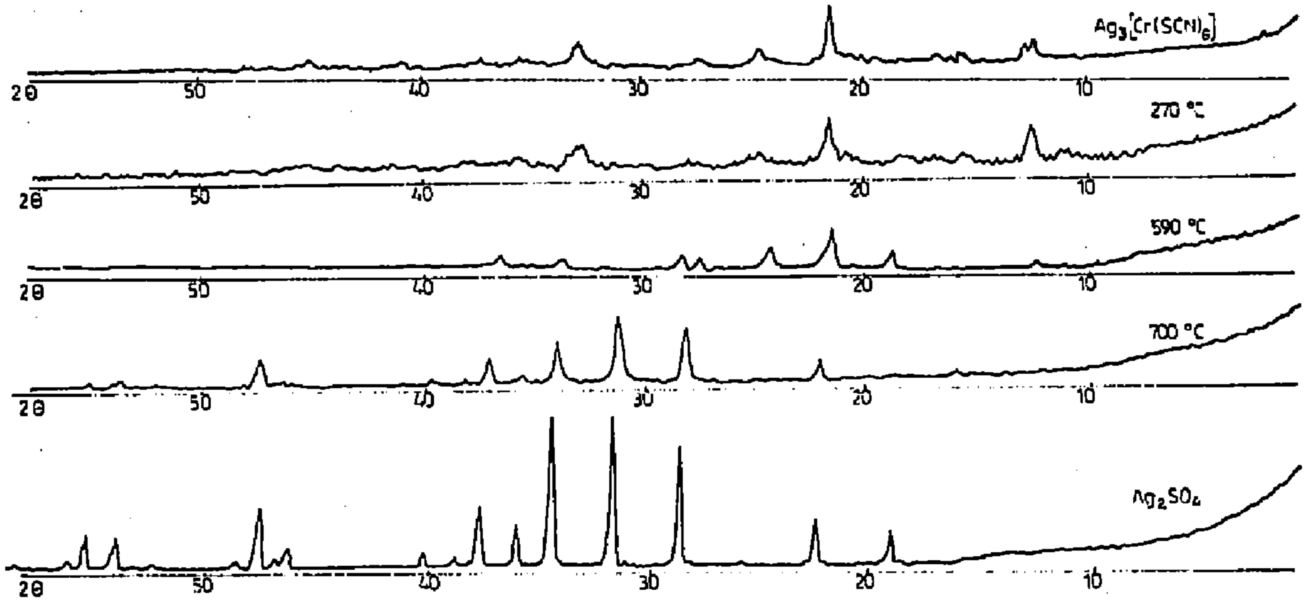

Fig. 4. X-ray diffraction patterns of Ag$_3$[Cr(SCN)$_6$], sinters and Ag$_2$SO$_4$.

8% is visible. At higher temperatures (700–1000°C) the mass of the sample does not change.

The course of the thermal decomposition reactions of the hexathiocyanatochromates under study was followed by heating the samples of about 100 mg of these compounds in a silite furnace at 5° min^{-1} in air (i.e. the conditions were similar to those under which the thermal analysis curves were prepared) up to appropriate temperatures determined from the TG curves. Sinters of Ag$_3$[Cr(SCN)$_6$] were prepared at 270, 390 and 700°C, of Tl$_3$[Cr(SCN)$_6$] at 450°C and of Hg$_3$[Cr(SCN)$_6$]$_2$ at 800°C. The samples tested were those whose changes in mass were similar to those calculated

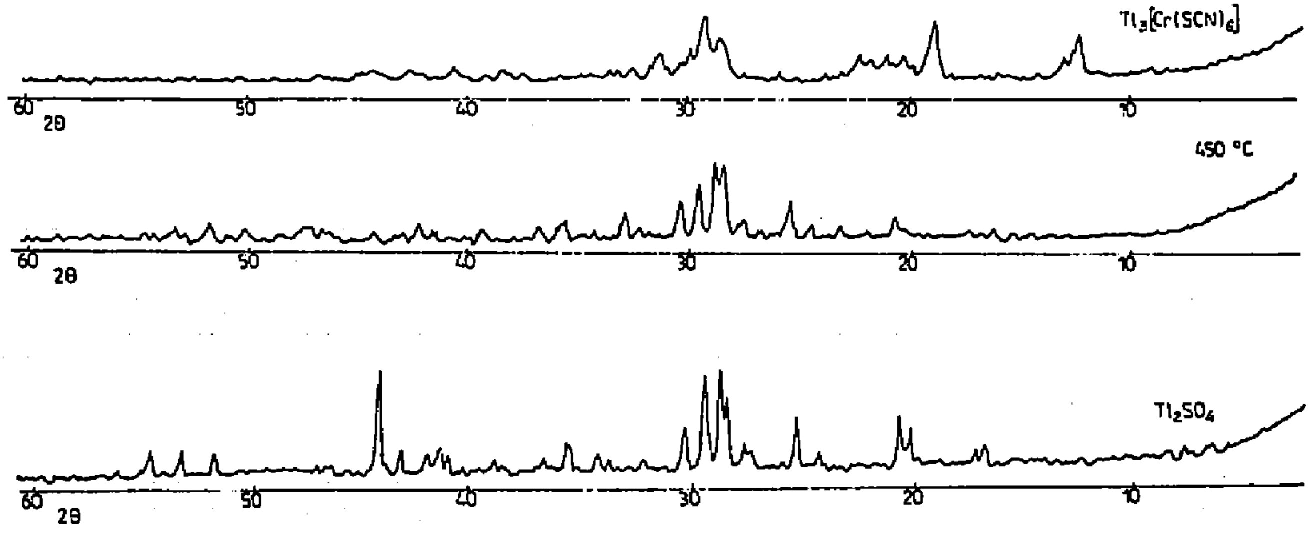

Fig. 5. X-ray diffraction patterns of Tl$_3$[Cr(SCN)$_6$], sinters and Tl$_2$SO$_4$.

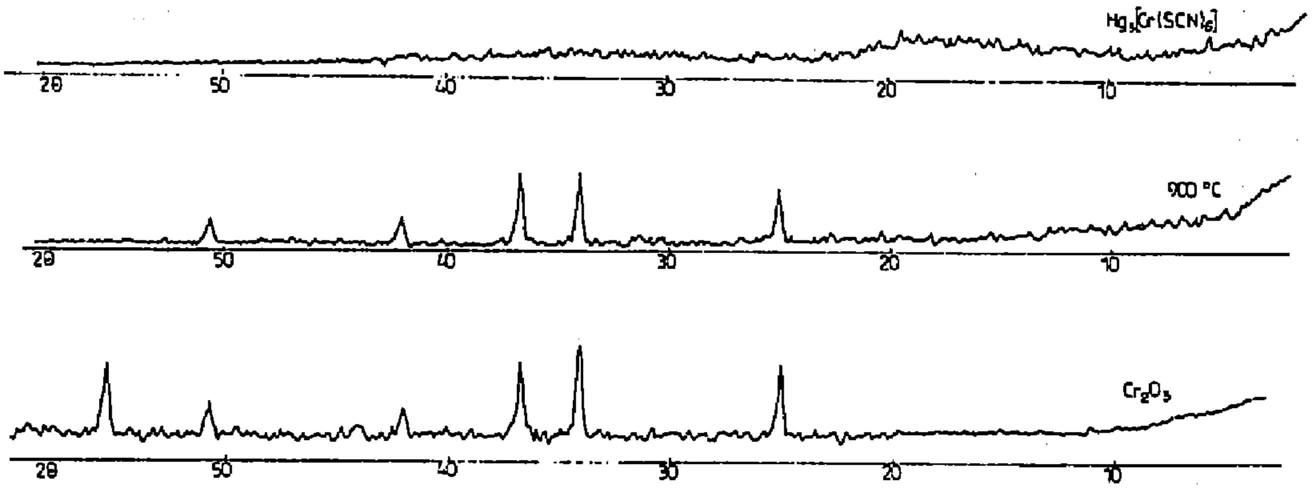

Fig. 6. X-ray diffraction patterns of $Hg_3[Cr(SCN)_6]_2$, sinters and Cr_2O_3.

TABLE 3

Kinetic parameters of the decomposition reactions of silver, thallium and mercury hexathiocyanatochromate(III) salts

Compound	Coats and Redfern [a]		Zsako [b]	
	E (kJ mol^{-1})	*n*	*E* (kJ mol^{-1})	*n*
$Ag_3[Cr(SCN)_6]$	68.5	0.3	71.2	0.4
$Tl_3[Cr(SCN)_6]$	216.7	2.0	209.3	1.9
$Hg_3[Cr(SCN)_6]_2$	88.0	1.0	87.9	1.0

[a] Ref. 8. [b] Ref. 9.

from TG curves at appropriate temperatures. Chemical analyses of the sinters were carried out by the methods described earlier. Chromium was determined iodometrically [7]. The diffraction patterns of the original compounds and the sinters are shown in Figs. 4–6.

Activation energies and reaction orders of the thermal decomposition reactions of the compounds under study were calculated from TG curves using the methods of Coats and Redfern [8] and Zsako [9]. Computer programs were based on the mathematical formulae given by these authors. The final results of these calculations are listed in Table 3.

CONCLUSIONS

The sparingly soluble fine crystals of silver and thallium hexathiocyanatochromate(III) salts and amorphous mercury hexathiocyanatochromate(III) instantly separate from the mother solutions at room temperature. The thermal decomposition of these salts takes place around 200°C and is not preceded by melting of the samples. According to the thermal, chemical and X-ray analyses of the solid intermediate and final products of the decomposition of $Ag_3[Cr(SCN)_6]$ and $Tl_3[Cr(SCN)_6]$, crystalline silver sulphate, thallium sulphate, and amorphous Cr_2O_3 are formed, whereas crystalline Cr_2O_3 is the only solid product of the decomposition of $Hg_3[Cr(SCN)_6]_3$. The quantitative compositions of the gaseous decomposition products were not examined exactly. According to our tentative quantitative analysis and the available literature data, in the course of the thermal decomposition of the thiocyanatochromates under study SO_2, CO_2 and N_2 are probably liberated.

Chemical and X-ray analysis of sinters obtained by heating the complex salts examined to the appropriate temperatures determined from the TG curves allow the following summary schemes of thermal decomposition reactions to be suggested.

$$2Ag_3[Cr(SCN)_6] \rightarrow 3Ag_2SO_4 + Cr_2O_3 + \text{gaseous products}$$

$$2Tl_3[Cr(SCN)_6] \rightarrow 3Tl_2SO_4 + Cr_2O_3 + \text{gaseous products}$$

$$Hg_3[Cr(SCN)_6]_2 \rightarrow Cr_2O_3 + \text{gaseous products}$$

The thermal stabilities of the compounds under study (defined by the temperature at which the decomposition starts) increase in the order $Hg_3[Cr(SCN)_6]_2 < Ag_3[Cr(SCN)_6] < Tl_3[Cr(SCN)_6]$. The activation energy of the thermal decomposition reaction of $Tl_3[Cr(SCN)_6]$ (about 210 kJ mol^{-1}) is distinctly greater than that of $Ag_3[Cr(SCN)_6]$ (about 71 kJ mol^{-1}) or that of $Hg_3[Cr(SCN)_6]_2$ (about 88 kJ mol^{-1}).

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