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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA
XIX. STUDY OF THE THERMAL DECOMPOSITION OF SOME HEXATHIOCYANATOCHROMATES

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Ammonium and metal salts of the acid $H_3[Cr(NCS)_6]$ have been obtained and characterized. Their thermal decomposition has been studied with a derivatograph. The thermal decomposition of the ammonium salts begins with an endothermic stage, leading to the formation of the intermediate $Cr(NCS)_3$, which in exothermic processes finally yields Cr_2O_3. The decomposition of the metal salts is exothermal and the polarizing effect of the cation plays an important part in this. Kinetic parameters have been derived by means of the nomogram method.

Hexathiocyanatochromic acid, $H_3[Cr(NCS)_6]$, forms numerous salts with metals, metal(II),(III)-amines and organic bases of various types. The alkaline and alkaline earth metals from derivatives that are readily soluble in water. The majority of the transition metal salts and those of the metalamines are only very slightly soluble in water, but soluble in some polar organic solvents [1–3]. The Ag, Pb and Bi salts have been used for the gravimetric determination of these metals. Certain metal-amine hexathiocyanatochromates can be used for the isolation and characterization of some very readily soluble complex cations [4–6].

Like the Reinecke acid $H[Cr(NCS)_4(NH_3)_2]$, $H_3[Cr(NCS)_6]$ also forms characteristic crystalline salts with organic tertiary N-bases and phosphines, having the general formulae $(\text{amine} \cdot H)_3[Cr(NCS)_6]$ and $(\text{phosphine} \cdot H)_3[Cr(NCS)_6]$. These water-insoluble salts can be used for the gravimetric, oxidimetric and spectrophotometric determination of some N-bases of pharmaceutical and biological importance. It is worth mentioning that the analogous derivatives with aromatic amines are generally resinous masses with no well-defined composition.

The thermal degradation of some $(\text{amine} \cdot H)_3[Cr(NCS)_6]$ and some metal(III)-amine derivatives of this type has been investigated by simple thermogravimetry by Ripan *et al.* [7–10].

During the pyrolysis of the latter derivatives N_2, CO, CO_2, SO_2, sulfur, carbon, amines, HCNS, etc. are formed in non-stoichiometric amounts. These compounds are stable up to 160–220°, the thermal stability being determined by the nature of the complex cation. The final product of the decomposition of the hexamine-, monoacidopentamine- and diacido-tetramine-cobalt(III) derivatives at 750–800° is a stoichiometric mixture of $Co_3O_4 + Cr_2O_4$ ($1/3\ Co_3O_4 + 1/2\ Cr_2O_3$, 3/4 Co_3O_4 + 1/2 Cr_2O_3, and Co_3O_4 + 1/2 Cr_2O_3, respectively). The formation of stoichiometric intermediates was not observed in the TG curves of these substances.

In the case of the thermal degradation of the amine salts one can presume the formation of $H_3[Cr(NCS)_6]$ and $Cr(NCS)_3$ as labile intermediates if the amine components are volatile [9, 10].

In the present paper the thermal decomposition of three ammonium and five metal salts of the acid $H_3[Cr(NCS)_6]$ has been studied with a derivatograph. The thermal curves are shown in Figs 1–2. As may be seen from these Figures, the general features of the thermal decomposition are rather different for the ammonium salts as compared to the metal salts.

In the case of the ammonium salts the thermal decomposition leads to the formation of the not very stable intermediate $Cr(NCS)_3$, i.e. in the first stage amine and HNCS are volatilized and lost. This reaction is marked by one or two endothermal peaks in the DTA curve (see Table 1). The decomposition of $Cr(NCS)_3$ is not a one-step process: it consists of the superposition of several exothermal processes, obviously oxidation reactions with the participation of atmospheric oxy-

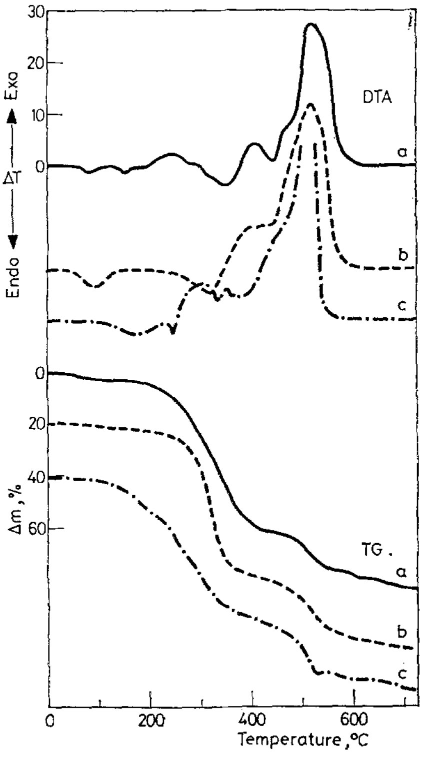

Fig. 1. TG and DTA curves a = $(PyH)_3[Cr(NCS)_6]$; b = $(\alpha\text{-picH})_3[Cr(NCS)_6]$; c = $(NH_4)_3[Cr(NCS)_6]$

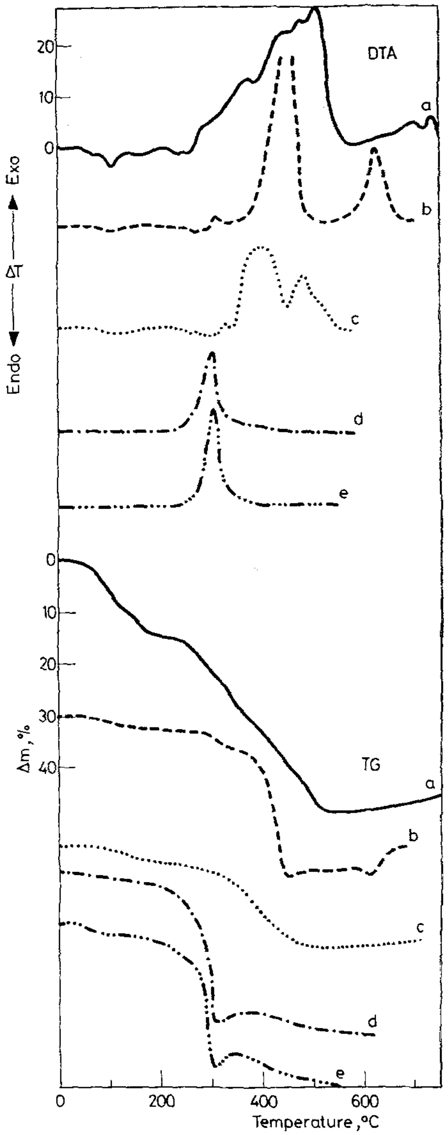

Fig. 2. TG and DTA curves a = $K_3[Cr(NCS)_6] \cdot 4\,H_2O$; b = $Ag_3[Cr(NCS)_6]$; c = $Tl_3[Cr(NCS)_6]$; d = $Bi[Cr(NCS)_6]$; e = $Pb_3[Cr(NCS)_6]_2$

gen. The last and largest exothermal peak appears at 510–520°. The final product of these reactions is Cr_2O_3 and the mass of the sample attains the corresponding value at about 750°.

The behaviour of the metal salts is characterized by the absence of endothermal peaks, except for the potassium salt, which gives a crystallohydrate with 4.5 moles

Table 1

DTA peak temperatures (°C) at the thermal decomposition of $M_3[Cr(NCS)_6]$ type complexes (the temperature of the most important peak is underlined)

M	Endothermic peaks		Exothermic peaks					Heating rate, degree/min
pyridine · H	280	350		398	480	$\underline{520}$		10
α-picoline · H	320			400	430	$\underline{520}$		10
NH_4	260	350				$\underline{510}$		10
K	100	160	370	440	470	$\underline{510}$	700	10
Ag	—				310	$\underline{460}$	620	10
Tl	—		275	325	$\underline{395}$	480	650	10
1/2 Pb	—				205	$\underline{305}$		2
1/3 Bi	—					295		2

H_2O; this loses its crystallization water in two steps, corresponding to two endothermal peaks at 100 and 160°, respectively. The anhydrous salts decompose only through exothermal reactions, leading to no well-defined intermediates. The highest exothermal peak is situated at 510° with the potassium salt, exactly as in the case of the ammonium salt, but it is shifted towards lower temperatures if the potassium ion is substituted by other ions with higher polarizing effects. This shift increases with increasing charge and with decreasing radius of the outer sphere cation, as seen from the data presented in Table 1.

Since the heating rate used was not the same for all the substances, in the case of the Pb and Bi salts the shift indicated in Table 1 is a little exaggerated. At a

Table 2

Characteristics of TG curves

Cation	Decomposition stage	Characteristic temperatures, °C			
		$t_{0.1}$	$t_{0.5}$	$t_{0.9}$	t_m
(pyridine · H)$^+$	endo	232	320	378	340
(α-picoline · H)$^+$	endo	274	315	348	315
NH_4^+	endo	140	255	338	280
(pyridine · H)$^+$	exo	465	510	550	500
(α-picoline · H)$^+$	exo	444	500	540	505
NH_4^+	exo	427	495	520	500
K^+	exo	265	376	485	490
Ag^+	exo	388	425	460	430
Tl^+	exo	337	395	460	370
Pb^{2+}	exo	267	290	308	300
Bi^{3+}	exo	258	285	300	280

heating rate of 10°/min the shift would be smaller by about 10–20°, but this does not affect the validity of the above-mentioned rule.

After these exothermal decomposition processes, leading to a minimum weight of the sample, a weight gain begins; this is also marked by exothermal peaks in the case of the K, Ag and Tl salts, and the weight of the final product corresponds to a stoichiometric mixture of $Cr_2O_3 + M_2SO_4$. The Pb and Bi salts do not show an exothermal effect at the weight gain. This is probably due to the instability of the corresponding sulphates at this temperature. This is why, after a maximum weight, a weight loss again appears in the TG curves.

Since the TG curves of the ammonium salts show two, and those of the metal salts one relatively well-defined decomposition stage, an attempt has been made to derive kinetic parameters for these decomposition stages. To this end a nomogram method [12] was used.

The results are given in Table 2. This Table contains the characteristic temperatures of the TG curves, *viz.* the temperatures corresponding to the conversion values 0.1, 0.5 and 0.9, as well as the temperature of the maximum decomposition rate t_m; the shape and position parameters defined as

$$\nabla = \frac{\vartheta_{0.5} - \vartheta_{0.9}}{\vartheta_{0.1} - \vartheta_{0.9}}, \quad \Delta = 10^6(\vartheta_{0.1} - \vartheta_{0.5}), \quad \tau = 10^3\vartheta_{0.1},$$

where ϑ_α stands for the T_α^{-1} values (reciprocal absolute temperature corresponding to the conversion α); and the kinetic parameters n, E and Z, i.e. the apparent reaction order, activation energy and pre-exponential factor.

As may be seen from this Table, in the case of the exothermal stage a systematic decrease of $t_{0.9}$ and t_m can be observed with increasing polarizing effect of the cation. A similar tendency is shown by $t_{0.1}$ and $t_{0.5}$, with a single exception: the

and kinetic parameters

Shape and position parameters			Kinetic parameters		
∇	Δ	τ	n	E, kJ/mol	$\log Z$, s^{-1}
0.338	294	1.980	0.57	41.2	0.8
0.417	127	1.828	1.22	117.9	8.2
0.328	527	2.421	0.49	20.8	−0.2
0.443	78	1.355	1.46	201.5	11.2
0.388	101	1.395	0.96	141.0	7.1
0.244	127	1.429	−0.17	90.7	3.3
0.411	318	1.859	1.23	42.0	0.6
0.463	80	1.513	1.66	205.1	13.2
0.484	142	1.639	1.88	115.9	6.7
0.420	76	1.852	1.24	203.0	16.2
0.341	91	1.883	0.56	150.8	11.2

K salt. The anomalous behaviour of the potassium salt is due to its crystallization water content. This water is released between 100 and 170° and the loose structure of the resulting crystals allows the thermal decomposition of the anhydrous salt to begin at lower temperatures than with compact crystals, and $t_{0.1}$ and $t_{0.5}$ will be lower than expected.

The position parameter τ of the exothermal stage shows a systematic increase with increasing polarizing effect of the cation, again except for the K salt.

The shape parameters and the kinetic parameters display no systematic variation and no special conclusions can be drawn.

Experimental

$K_3[Cr(NCS)_6 \cdot 4.5\,H_2O$ and $(NH_4)_3\,[Cr(NCS)_6]$ were obtained by evaporating to dryness a mixture of 0.1 mole $KCr(SO_4)_2 \cdot 12\,H_2O$ and 0.6 mole KCNS (or $(NH_4)Cr(SO_4)_2 \cdot 12\,H_2O + NH_4CNS$).

The residue was extracted with ethanol. The complex salts crystallize from alcoholic solutions.

Table 3

Analytical data on the $K_3[Cr(NCS)_6]$ type complexes

M	Mol. weight calcd.	Analysis		
		calcd.		found
(pyridine · H)	640.6	Cr	8.11	8.16
		N	19.68	19.87
		S	30.02	29.77
(α-picoline · H)	682.1	Cr	7.62	7.50
		N	18.47	18.75
		S	28.19	28.35
NH_4	454.4	Cr	11.44	11.54
		N	27.74	27.98
		S	42.33	42.67
K (4.5 H_2O)	598.7	Cr	8.68	8.62
		S	32.12	32.00
		H_2O	13.58	12.90
Ag	723.9	Cr	7.18	7.24
		S	26.57	26.86
Tl	1013.4	Cr	5.13	5.08
		S	18.98	19.23
1/3 Bi	609.3	Cr	8.53	8.68
		S	31.57	31.70
1/2 Pb	1422.1	Cr	7.32	7.25
		N	11.82	11.99

$Ag_3[Cr(NCS)_6]$, $Tl_3[Cr(NCS)_6]$, $Bi[Cr(NCS)_6]$ 3–4 g $AgNO_3$ or $TlNO_3$ was dissolved in 200 ml 0.1 *N* HNO_3 and treated with an excess of 2% $K_3[Cr(NCS)_6]$. The precipitated microcrystalline products were filtered and washed with water. $Bi[Cr(NCS)_6]$ was precipitated from a more acid solution (1*N* HNO_3) (scarlet crystalline product). (amine · $H)_3[Cr(NCS)_6]$ salts. 20 millimoles of the corresponding amines were treated with 5 ml conc. HCl and then dissolved in 60–100 ml water. The solutions were treated with an excess of 2% $K_3[Cr(NCS)_6]$. The violet microcrystalline products were separated and washed as in the above-mentioned cases.

The purities of the substances were established by determination of the chromium (iodometrically as CrO_4^{2-}), thiocyanate (gravimetrically as $BaSO_4$) and nitrogen (gas-volumetrically after Kjeldahl's method) contents. Analysis data are given in Table 3.

The measurements were carried out with a MOM derivatograph (Budapest). Sample weight: 100 mg. Atmosphere: static air. Reference material: α-Al_2O_3. Platinum crucible [11].

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Zusammenfassung — Ammonium- und Metallsalze der Säure $H_3[Cr(NCS)_6]$ wurden hergestellt und charakterisiert. Ihre thermische Zersetzung wurde mit einem Derivatographen verfolgt. Sie beginnt beiden Ammoniumsalzen mit einer endothermen Phase, welche zur Bildung des Zwischenprodukts $Cr(NCS)_3$ führt, das in exothermen Vorgängen als Endprodukt Cr_2O_3 ergibt. Die Zersetzung der Metallsalze ist exotherm und der Polarisationseffekt des Kations spielt hierbei eine wichtige Rolle. Kinetische Parameter wurden nach der Nomogramm-Methode abgeleitet.

Резюме — Получены и охарактеризованы аммониевые соли и соли металлов кислоты $H_3[Cr(NCS)_6]$. С помощью дериватографа изучено их термическое разложение. Разложение аммониевых солей начинается с эндотермической стадии, приводящей к образованию промежуточного продукта $Cr(NCS)_6$, который в экзотермическом процессе дает Cr_2O_3. Разложение других солей протекает по экзотермическому процессу и главную роль при этом играет поляризационное влияние катиона.