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STUDY ON THE THERMAL DECOMPOSITION OF CHROMIUM(III) NITRATE NONAHYDRATE (CNN)

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ABSTRACT

The stoichiometry of the thermal decomposition stages of CNN in the temperature range 20–500 °C was studied using TG, DTG and DTA, together with the chemical analysis of gaseous products formed during this process (EGA). The solid intermediates and final decomposition products of CNN, prepared by isothermal heating at desired temperatures, were characterized and identified by IR spectrometry, as well as by standard and indirect chemical analysis. On the basis of the results obtained, a probable mechanism for the overall decomposition of CNN in the above temperature range is proposed.

INTRODUCTION

Chromium oxide (α-Cr_2O_3) plays an important part in many industrial processes. It is widely used as an active phase and as a promoter in a variety of mixed oxide catalysts or as an excellent carrier material, due to its stable surface at high temperatures. Chromium oxide is usually obtained by the thermal decomposition of its salts and, therefore, this process constitutes a decisive step in its production. In most uses of Cr_2O_3 the detailed knowledge of the degradation processes of these salts is of great value.

Thermal studies of hydrated metal nitrates have often been the subject of investigations [1], but the decomposition of CNN has not been adequately studied, although its presumed decomposition products have been mentioned by several authors [2–10]. The results and opinions cited in the literature are, however, vague and not absolutely conclusive. In these reports a distinct disagreement about the formation of particular intermediates or their sequence of appearance and decay during the process is observed. The problem of the form of the evolved nitrogen compounds and the mechanism of the formation and decomposition of intermediate products of denitrification, oxidation and reduction of CNN and other compounds is also unresolved [2,4,8,9].

The main objective of the present study was, therefore, to identify the separate intermediates, to determine the precise temperature range of their

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existence and to establish the stoichiometries of various stages of this process. Apart from the standard thermal studies in static air, the decomposition has also been investigated using the constant air flow system. It enables the gaseous decomposition products either to be trapped out or collected in gas bulbs for subsequent identification, which gave complementary information about the reactions studied.

EXPERIMENTAL

Materials

The chemicals used, CNN and those for the chemical analysis, were all of Analar grade (POCh, Gliwice, Poland).

Thermal analysis

The behaviour of the samples was studied with an automatic Paulik–Paulik–Erdey derivatograph, manufactured by MOM (Budapest, Hungary). The following conditions were used: sample size, 0.1–0.5 g; reference material, α-Al_2O_3 (calcined at 1500 °C); sample holder, platinum crucible placed on a thermocouple rod; thermocouple, Pt/Pt–Rh; linear heating rate, 10 °C min^{-1}; temperature range, 20–500 °C; atmosphere, static air.

Solid decomposition products

In order to characterize the decomposition residue and to explain the course of the intermediate decomposition processes, pure samples of CNN were heated in a constant air flow at selected and well-controlled temperatures in a pipe furnace or in a distillation apparatus. The decomposition was performed until a constant sample weight was obtained. The gaseous decomposition products were absorbed in standard NaOH solution and the solid residues collected after each heat treatment were allowed to cool in air in a desiccator at room temperature and submitted to IR and chemical analysis.

IR analysis

Considering that the intermediate decomposition products are of roentgenographic amorphous character, the IR absorption measurements were at first adopted for their identification. IR spectra of the loose solid samples were recorded on an UR-20 Spectrometer (C. Zeiss, Jena, GDR) in the range 400–4000 cm^{-1}, using the 1%-KBr disc technique. For greasy materials, IR spectral examinations were made using a Specord 71 Spectrophotometer (C. Zeiss, Jena, GDR) equipped with an ATR (Attenuated Total Reflection) attachment described elsewhere [11], in the range 650–4000 cm^{-1} with the following conditions: Ge monocrystal plate, reflection angle $Q = 45°$, reflection frequency $N = 25$. The obtained spectra were compared with the standard spectra from the catalogue of Nyquist and Kagel [12] and from other sources.

Chemical analysis

The solid decomposition products were also characterized by wet chemical analysis. The total chromium content was determined iodometrically after oxidizing Cr^{3+} to Cr^{6+} by Na_2O_2 in aqueous alkaline solution (wet peroxide method) and destroying the excess oxidant by boiling [13] (best results with addition of nickel salt [14]). The content of the Cr^{6+} alone was also determined iodometrically after using the original procedure, based on hot leaching of the samples with 4 N NaOH solution and filtration of insoluble residue. The samples not solubilized in the wet peroxide method were oxidized by fusion with Na_2O_2 in a Ni crucible. The content of Cr^{3+} in all products was calculated as the difference from total chromium and Cr^{6+} percentages. The OH^- ions were analysed using Lehigh's [13], Steinhauser's [15] or Kalbus and Petrucci's [16] methods, and NO_3^- ions by the back titration of the excess of standard H_2SO_4 solution in ammonia distillate, obtained after reduction of nitrates with Devarda's alloy [17]. The water content in the residues was estimated from the difference to 100% of the other results. The phase compositions of residues were calculated by means of an original, indirect method, based on the results of the determination of common ions and on stoichiometric relations between CNN and its possible decomposition products.

The HNO_3 evolved during calcination of samples was determined by absorbing the gases produced in 1 N NaOH standard solution and titration of its excess with 0.5 N H_2SO_4 standard solution.

The relative errors in particular analyses were of the order 1–2%.

RESULTS AND DISCUSSION

Thermal analysis

The course of the thermal curves (Fig. 1) indicates that the thermal dissociation of CNN proceeds, essentially, in four successive stages. The DTA curve of the sample exhibits three endothermic peaks at 60, 150 and 160 °C, and one exothermic peak at 420 °C. The DTG curve proves that, except for the first one, all other effects are accompanied by weight losses of the sample. Thus, the first stage, at 60 °C, is characterized by the endother-

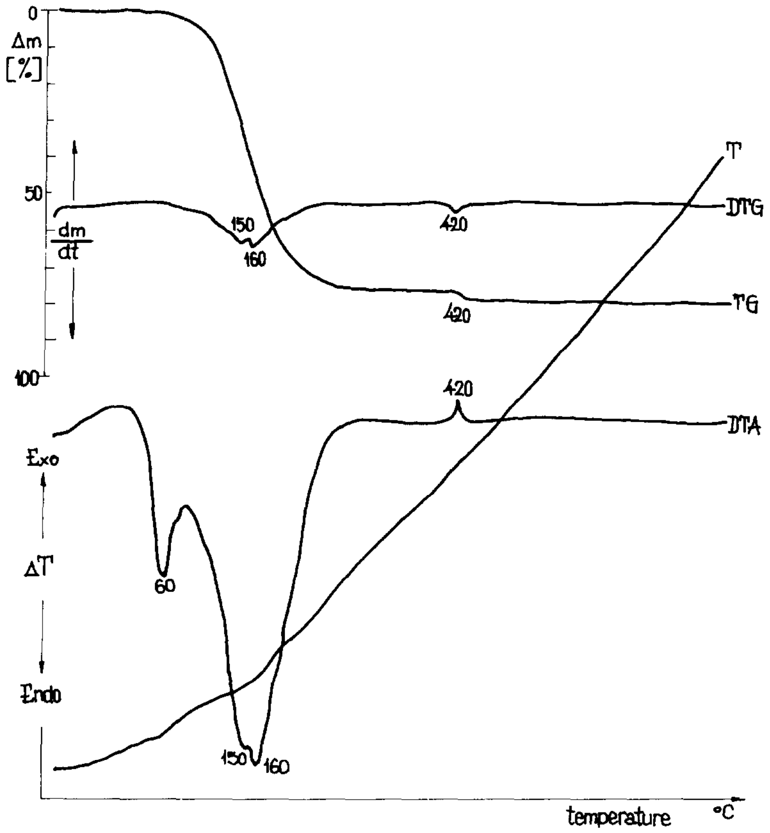

Fig. 1. Thermal analysis curves of CNN in air.

mic peak on the DTA curve without the corresponding features on the DTG curve. This stage is elucidated as the melting process of CNN. According to data [18], the melting point of CNN is really 60 ° C. The melted CNN forms a green-coloured liquid. Near to the melting point of CNN continuous weight loss begins, which persists, according to the TG curve, until 420 ° C.

The second stage of CNN decomposition, connected with the endothermic peak at 150 ° C on the DTA curve and with the minimum on the DTG curve at this temperature, involves the formation of an intermediate product. The nature, the course of formation and the temperature range of its existence are, however, undefined and unknown. According to our EGA measurements, the initial phase of CNN decomposition consists in the slow formation and evaporation of nitric acid. The origin of its formation is the thermal hydrolysis of the melted CNN, determined by the weak basic character of the Cr^{3+} cations. This conversion occurs very slowly from 60 ° C upwards and at a noticeable rate from about 102 ° C. The vigorous evaporation of HNO_3 corresponds to the region of about 120.7 ° C, i.e. the boiling point of the azeotropic mixture HNO_3–H_2O [18]. The elimination of gaseous HNO_3 from the CNN melt suggests that, in the residue, basic chromium nitrates are accumulated. The quantities of HNO_3 evolved at 130 and 150 °C are indicative of the formation of mixtures of mono- and dibasic chromium nitrates. This reaction appears to be complete at 150 °C, with the formation of a dark-green, amorphous, solid product, which is very hygroscopic and soluble in water, ethanol or acetone.

In the third stage of CCN decomposition, an endothermic effect on the DTA curve appears at a temperature of 160 °C, along with a simultaneous negative peak on the DTG curve. The EGA results indicate the liberation of a gaseous HNO_3 and NO_2 mixture, which shows that the denitrification of CNN is a two-stage process, containing, besides the distillation of the HNO_3, the evolution of its reduction product, i.e. the redox process, leading to oxidation of Cr^{3+}. It is demonstrated by the formation of a dark-brown residue in this stage, which is only partially soluble in water and in organic solvents. The endothermic character of this stage is probably due to the partial decomposition of basic chromium nitrates.

Scarce literature data [4,7] report the existence of only one decomposition step in this region, namely at 160 °C, comprising the simultaneous boiling of CNN and then its dehydration and denitrification. According to another opinion [18] the temperature of 125.5 °C is accepted as the boiling point of CNN. At this temperature the total decomposition of the salt takes place. Besides the temperature values given above, the total decomposition of CNN is ascribed to a range of 152–172 °C [2], and even to above 200 °C [10], and corresponds to the formation of Cr_2O_3 only.

The fourth stage in the CNN decomposition comprises the exothermic effect on the DTA curve and the weight loss, both at 420 °C, as well as the negative peak on the DTG curve. These last effects can be probably attributed to the removal of oxygen and water, decomposition of intermediate compounds and formation of the final product. The review of available literature shows that the mentioned reactions have not been studied so far. The origin of the exothermic effect at 420 °C has also not been examined. The situation described requires additional analytical work.

IR analysis

In order to obtain more information about the chemical changes induced by heat in the CNN substrate, IR spectra were taken of products isothermally calcined at different temperatures. The choice of these temperatures was related to the weight and energy changes, deduced from the thermal curves of CNN. The results of IR analysis for all products are reported in Fig. 2. The perceptible change in the CNN spectrum, caused by prolonged heating (205 h) at 60 °C, results in the diminution of the intensity of the absorption band at 1385 cm^{-1}, assigned to NO_3^- ions [18–21], which fact

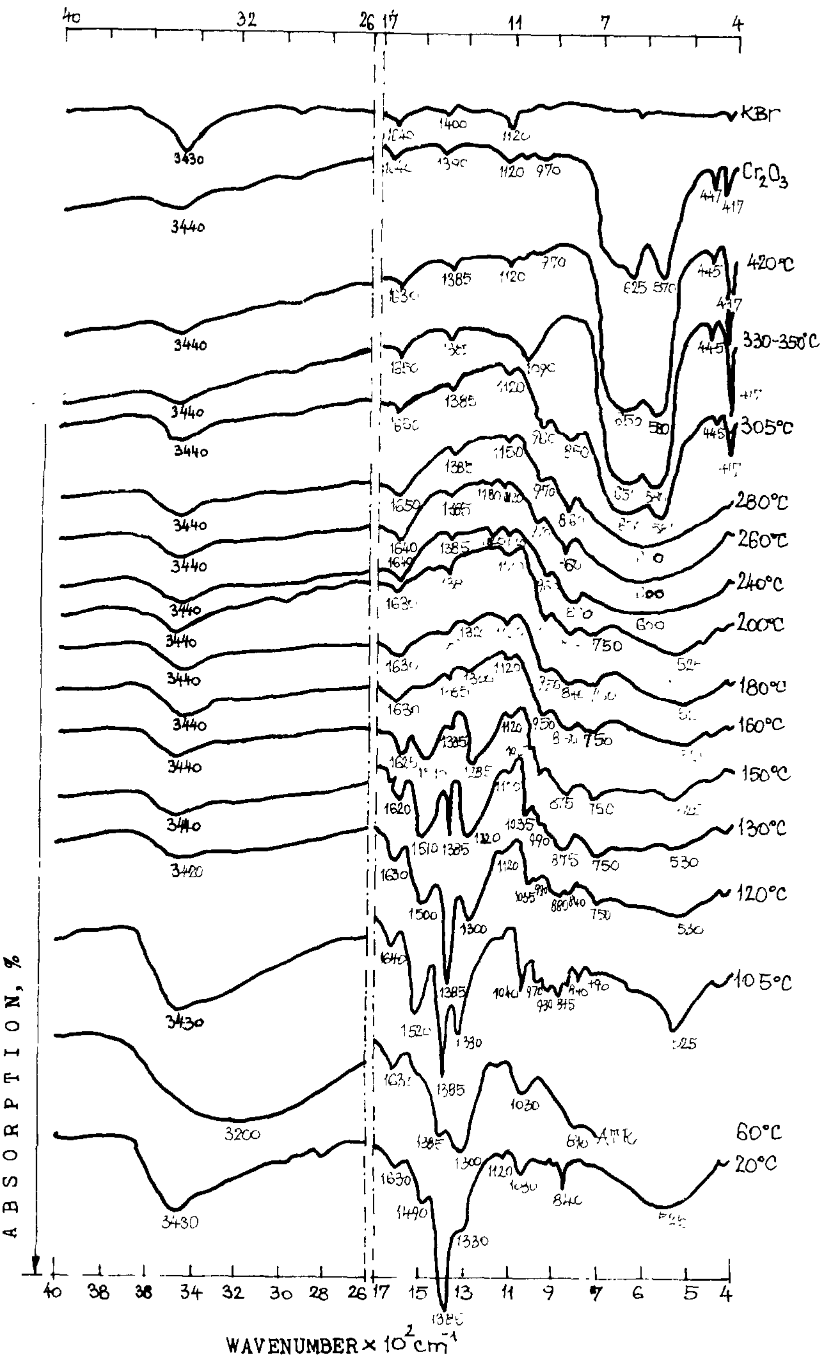

Fig. 2. IR spectra of CNN and its calcination products at the temperatures indicated (KBr disc technique).

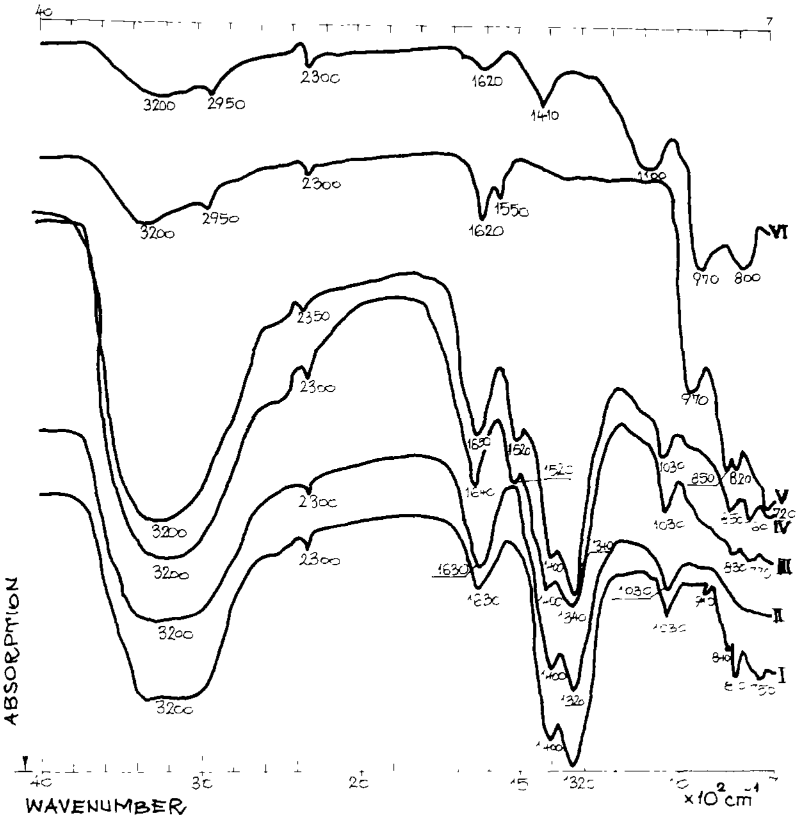

Fig. 3. Reference IR spectra of hypothetical intermediate CNN decomposition products (obtained by ATR technique): I, tails after distillation of 1 mol of HNO_3 from 1 mol of CNN melt; II, product of reaction ($Cr(OH)_3 + 2Cr(NO_3)_3 \rightleftharpoons 3CrOH(NO_3)_2$); III, tails after distillation of 2 mol of HNO_3 from 1 mol of CNN melt; IV, product of reaction ($2Cr(OH)_3 + Cr(NO_3)_3 \rightleftharpoons 3Cr(OH)_2NO_3$); V, $CrOHCr_2O_7 \cdot 2H_2O$ prepared according to ref. 38; VI, $[Cr(OH)_2]_2CrO_4$ prepared according to ref. 39.

confirms the beginning of their decay. The course of this decomposition is elucidated by the IR spectrum of the residue after heating CNN at 105 ° C, containing, on the one hand, the absorption bands at 1030–1040, 1285–1330 and 1500–1520 cm^{-1}, which exist in the reference IR spectra of basic chromium nitrates (Fig. 3), and, on the other hand, a series of absorption bands in the region of 700–1000 cm^{-1}, which are assigned to chromates [12,21–25]. In addition, the separate bands between 700–800 cm^{-1} indicate the presence of bichromates as well as chromates [21,26]. The band at 525–530 cm^{-1}, connected, in the opinion of Sakharova et al. [27], with the valence vibration of the Cr^{3+}–O bond, suggest the existence of Cr(III) salts in the residue. The bands at 1030–1040 cm^{-1}, derived, according to Kalinichenko et al. [3], from the deformation vibration of the Cr–OH bond and the band at around 3400 cm^{-1}, resulting from the plane OH vibration [28], would suggest the existence of chromium nitrates, bichromates and chromates in the residue in the form of basic salts. With an increase in temperature of CNN decomposition to 120 and 130 ° C, the IR absorption spectra obtained are very similar to those at 105 ° C, except for the diminution of intensity of the absorption band at 1385 cm^{-1}, connected with a further decrease of nitrate content, and the diminution of a number of bands in the range 700–1000 cm^{-1}, unexplained in the literature. The band at 1330 cm^{-1} is also shifted in frequency to 1300 and 1290 cm^{-1} with a simultaneous decrease of its intensity. With the subsequent rise of the temperature to 150 ° C, further diminution of intensity of the 1385 cm^{-1} band in the spectrum of the residue was marked, showing the continuous decrease of nitrate content with increase of the decomposition temperature. Thus, the endothermic reaction between 125 and 150 ° C is associated with the partial decomposition of these ions. The next change in the absorption pattern is observed for the decomposition product at 160 ° C and is the disappearance of the bands at 1030–1040, 1285 and 1510–1520 cm^{-1}, found also in reference IR spectra of isolated basic chromium nitrates (Fig. 3). This confirms the decay of the dibasic chromium nitrate. From this temperature, the principal constituents of the CNN decomposition products are basic chromium chromates. Such a composition of residues is maintained also at higher temperatures in a range of several dozens of degrees. Only in the residue spectrum at 240 ° C can the decay of the band at 750 cm^{-1} and displacement of the band at 525 cm^{-1} to a frequency of 600 cm^{-1} be observed. The origin of this displacement of the maximum of valence vibration of the Cr^{3+}–O bond to a higher frequency is ascribed either to the condensation of the neighbouring OH-groups [27] or to its conversion into the oxide form [28]. Thus, the residue after calcining of CNN at 240 ° C can be probably assigned to the normal chromium chromate. The absorption bands, characteristic for this compound (600, 850–860 and 960–970 cm^{-1}) are maintained in the absorption spectra of the residues after calcining at temperatures up to 305 ° C and disappear only at 330–350 ° C.

In the temperature range 170–300 ° C some authors suggest the existence of oxides corresponding to intermediate valencies of chromium, namely CrO_2 [9,10] and Cr_2O_5 [10] in the decomposition products of CNN. The IR absorption spectra of these compounds, described in the literature (refs. 29, 30 and 26, respectively), contain the absorption bands at 530 and 700–1000 cm^{-1}, similar to those obtained in our measurements of CNN decomposition products. The data cited confirm the older suppositions [31,32] that the mentioned oxides are in fact chromium polychromates of different composition. It is worth mentioning that the X-ray photoelectron spectrum of Cr_2O_5, obtained by Tsutsumi and co-workers [33] also indicates that the chromium ions in this compound are not in the Cr^{5+} state, but in a mixed valence state consisting of Cr^{6+} and Cr^{3+}, presumably in the ratio of 2 : 1. Similar conclusions are postulated from the measurements of IR absorption, EPR and XRD spectra of Cr_2O_5 and Cr_3O_8, performed by Hewston and Chamberland [26].

The IR absorption spectrum of the CNN decomposition product at 305 ° C, besides the absorption bands of chromium chromate, exhibits new bands at 417, 445, 580 and 625–650 cm^{-1}, typical of Cr_2O_3 [12,34,35], indicating that, in these conditions, the conversion of chromium chromate to Cr_2O_3 is started. This conversion lasts to 420 ° C. The absorption bands of the residue after calcining at this last temperature correspond to the standard spectrum of Cr_2O_3. The nature of this product was confirmed with the help of X-ray diffractometry using nickel-filtered Cu–K_α radiation. The data obtained correspond to the ASTM Powder Diffraction File 6-0504 for Cr_2O_3.

Chemical analysis of the solid CNN decomposition products

For the accurate definition of the chemical composition of the residues after isothermal CNN decomposition at different temperatures, a determination of the Cr^{3+}, Cr^{6+}, NO_3^- and OH^- contents was performed. The results of these analyses are presented in Table 1. The existence of OH and NO_3 groups, as well as Cr(VI) compounds at 130 ° C confirms the IR spectrometry data, i.e. the formation of basic chromium nitrates, bichromates and chromates. With a further rise of temperature to 240 ° C, the Cr^{6+} contents increases to a maximum with simultaneous decrease of the Cr^{3+}/Cr^{6+} ratio. This relationship is, however, irregular and the minima of it are observed, which can be explained by different mechanisms of the oxidation processes operating in particular temperature ranges. Thus, the distillation of HNO_3 to

TABLE 1

Results of chemical analysis of the CNN decomposition products at different temperatures

Heating temperature (° C)	Heating time (h)	Weight loss (%)	Composition (%)			
			Cr^{3+}	Cr^{6+}	OH^-	NO_3^-
130	100	70.9	24.38	20.46	8.60	20.76
150	75	75.5	24.57	24.64	9.58	10.12
160	83	76.2	29.57	22.35	11.05	4.93
180	48	76.8	29.10	22.87	10.05	2.05
200	60	77.1	26.62	27.85	7.90	–
240	45	77.6	24.33	31.10	–	–
260	48	77.8	24.70	30.58	–	–
280	40	78.0	25.41	30.22	–	–
305	40	79.5	46.82	15.86	–	–
330	48	80.0	66.22	1.10	–	–
420	58	80.9	67.17	0.38	–	–

150 ° C suggests that, in this region, the oxidizing agent may be the boiling acid. The evolution of gaseous NO_2 at 160–170 ° C is, however, connected with the decay of the basic chromium nitrates. Above the temperature of 180 ° C, in the absence of nitrates in residues, the oxidation of Cr^{3+} may be performed only as an effect of aerial oxygen. The maximum Cr^{6+} content in CNN decomposition products observed at 240 ° C is maintained up to 280 ° C at a similar level. At 305 ° C a sharp decrease of Cr^{6+} occurs, accompanied by an increase in Cr^{3+} content. With a further rise of temperature to 420 ° C, the decay of Cr^{6+} compounds to almost zero is observed. The Cr^{3+} content in this product corresponds to the value in Cr_2O_3. In Table 1 the values of experimental weight losses are also presented at different isothermal decompositions of CNN. The elevation of temperature results in a gradual increase of the loss to a value of about 81%, corresponding to the conversion of CNN to Cr_2O_3.

For the qualitative and quantitative elucidation of the phase composition of the CNN decomposition products at particular temperatures an indirect chemical analysis was performed, based on material balance of the results of the determination of common ions and on the Cr^{3+}/Cr^{6+} ratios and so-called "theoretical weight losses" at calculated phase compositions. The results of the indirect analysis, presented in Table 2, generally confirm the conclusions derived from the IR absorption measurements of CNN decomposition products at various temperatures, and allow for additional precise

TABLE 2

Phase composition of the residues after isothermal CNN decomposition

Heating temperature (° C)	Cr^{3+}/Cr^{6+} ratio (except nitrate)	Composition (%)			
		$CrOH(NO_3)_2$	$Cr(OH)_2NO_3$	$CrOHCr_2O_7$	$CrOHCrO_4$
120	0.72	28.83	5.34	31.41	32.00
150	0.67	1.28	22.20	45.00	29.23
160	1.14	–	11.77	–	68.56
180	1.20	–	4.89	–	65.32
200	0.96	–	–	–	85.97
240	0.78	–	–	–	–
260	0.81	–	–	–	–
280	0.84	–	–	–	–
305	2.95	–	–	–	–
330	60.20	–	–	–	–
420	176.76	–	–	–	–
Theoretical weight loss for separate compound (%)		51.0	63.0	76.3	76.9
Cr^{3+}/Cr^{6+} ratio for separate compound		0.0	0.0	0.5	1.0

determinations of the degree of basicity of particular salts and their quantitative ratios.

Chemical reactions involved in the thermal CNN decomposition

Stage 1. The CNN begins to decompose after its melting point around 60 ° C (the CNN decomposition below its melting point has not been discussed at present). This stage contains the endothermic phase transition (melting) and also the endothermic process of thermal hydrolysis of melted CNN, represented by the equation:

$$2Cr(NO_3)_3 \cdot 9H_2O \rightleftharpoons CrOH(NO_3)_2 + Cr(OH)_2NO_3 + 3HNO_3 + 15H_2O \quad (1)$$

Stage 2. CNN decomposition during this stage is also of endothermic character and proceeds in the range 100–150 ° C. From 102 ° C a distinct evaporation of HNO_3 is observed. Around 120 ° C the distillation of the azeotropic mixture HNO_3–H_2O takes place, resulting in the shift of the hydrolysis equilibrium to the right and formation of the product with the higher degree of basicity according to equation:

$$CrOH(NO_3)_2 + H_2O \rightleftharpoons Cr(OH)_2NO_3 + HNO_3 \quad (2)$$

The gaseous decomposition products in this stage are colourless and the residue after calcining is green. The boiling of the melt with the azeotrope can also result in the partial oxidation of Cr(III) compounds, at first

$Cr_2(OH)_4CrO_4$	$Cr_2(CrO_4)_3$	$Cr_2O_3 \cdot H_2O$	Cr_2O_3	H_2O	Weight loss for calculated phase composition (%)
–	–	–	–	2.42	71.9
–	–	–	–	2.29	76.3
17.05	–	–	–	2.62	75.8
24.97	–	–	–	4.82	76.5
–	10.67	–	–	3.36	77.1
–	90.08	5.85	–	4.07	77.1
–	88.58	7.06	–	4.36	77.7
–	87.55	8.60	–	3.85	77.7
–	45.97	–	52.97	1.06	79.5
–	3.16	–	95.71	1.13	80.9
–	1.10	–	97.80	1.10	81.0
75.6	77.4	78.8	81.0	–	–
2.0	0.667	∞	∞	–	–

according to eqn. (3), then (4),

$$3Cr(OH)_2^+ + 2NO_3^- \rightleftharpoons CrOHCr_2O_7 + 2NO + 2H_2O + H^+ \tag{3}$$

$$2Cr(OH)_2^+ + NO_3^- \rightleftharpoons CrOHCrO_4 + NO + H_2O + H^+ \tag{4}$$

and causes the formation of basic chromium dichromates and chromates. This stage comes to an end with the complete evaporation of liquid and stopping of the distillation at about 150 ° C.

Stage 3. The subsequent stage of the CNN decomposition, observed in the range 150–60 ° C, is also associated with the endothermic reactions. Here, the symptom of the chemical conversion is the evaporation of the HNO_3–NO_2 gaseous mixture (brown fumes) and formation of a brown residue, partially insoluble in water. The chemical reactions may be represented by eqns. (2) and (4), then by eqns. (5) and (6):

$$3Cr(OH)_2NO_3 \rightleftharpoons [Cr(OH)_2]_2CrO_4 + 3NO_2 + H_2O \tag{5}$$

$$CrOHCr_2O_7 + Cr(OH)_2NO_3 \rightleftharpoons 2CrOHCrO_4 + HNO_3 \tag{6}$$

The resultant character of these conversions is endothermic and induces the negative peak on the DTA curve.

Stage 4. In the temperature range 170–420 ° C no thermal effect on the DTA curve has been found, marking the apparent absence of chemical reactions. However, from the IR absorption measurements and from the results of indirect chemical analysis the formation and decay of other chromium compounds is evident, which may be ascribed to further chemical processes. These facts show the presence of additional steps in this temperature range. Thus, the diminution of the $Cr(OH)_2NO_3$ content and the increase of the $[Cr(OH)_2]_2CrO_4$ ratio in the calcining product at 180 ° C may be illustrated by the equation:

$$CrOHCrO_4 + Cr(OH)_2NO_3 + H_2O \rightleftharpoons [Cr(OH)_2]_2CrO_4 + HNO_3 \tag{7}$$

At 200 ° C the aerial oxidation of basic chromium chromates starts. The $[Cr(OH)_2]_2CrO_4$ is first transformed into $CrOHCrO_4$, according to eqn. (8), and then partially oxidized into the normal chromium chromate, according to eqn. (9):

$$4[Cr(OH)_2]_2CrO_4 + \tfrac{3}{2}O_2 \rightleftharpoons 6CrOHCrO_4 + 5H_2O \tag{8}$$

$$20CrOHCrO_4 + 3O_2 \rightleftharpoons 8Cr_2(CrO_4)_3 + 10H_2O \tag{9}$$

In the range 200–240 ° C, the further course of reaction (9) is observed, resulting in the diminution of $CrOHCrO_4$ and in the increase of $Cr_2(CrO_4)_3$ content. The maximum value of the latter is obtained at 240 ° C. Simultaneously, small quantities of hydrated forms of Cr_2O_3 are recorded. Similar compositions of the CNN decomposition products were observed up to 280 ° C. This stage appears to be complete with the total conversion of substrates to normal chromium chromate.

Stage 5. At 305 °C a violent decomposition of the normal chromium chromate begins according to the equation:

$$2Cr_2(CrO_4)_3 \rightarrow 5Cr_2O_3 + \tfrac{9}{2}O_2 \qquad (10)$$

The conversion of $Cr_2(CrO_4)_3$ to Cr_2O_3 may be also described in the form of a gradual reduction of CrO_3 content in this compound in a sequence of several consecutive reactions:

$$Cr_2(CrO_4)_3 \rightarrow Cr_2O_3 \cdot 2CrO_3 \rightarrow Cr_2O_3 \cdot CrO_3 \rightarrow Cr_2O_3 \qquad (11)$$

From this series, Park [36] found the semicrystalline compound $Cr_2O_3 \cdot CrO_3$ as being the thermally stable phase at 310–70 °C. The IR spectrum of it (350 °C) monitors the coexistence of absorption bands of chromates (700–1000 cm^{-1}) and Cr_2O_3-like structures (300–700 cm^{-1}). Upon increasing the temperature up to 390 °C, $Cr_2O_3 \cdot CrO_3$ begins to lose its stability, undergoing a loss of its original weight due to released oxygen. Gravimetrically, this loss equals what one expects from the equation:

$$2Cr_2O_3 \cdot CrO_3 \rightarrow 3Cr_2O_3 + \tfrac{1}{2}O_2 \qquad (12)$$

Stage 6. This stage involves the exothermic effect on the DTA curve at 420 °C, probably explained by the formation of crystalline α-Cr_2O_3 from the amorphous product of reactions (10) or (11) and (12). Such a transformation on another occasion has been already described in the literature [27,37].

CONCLUSIONS

Thermal studies of CNN (TG, DTG, DTA, EGA), supplemented by IR and chemical analyses of the solid decomposition products from isothermal decomposition studies in the temperature range 20–500 °C, lead to the conclusion that the decomposition occurs in six stages and involves the following processes:

Stage 1

$T = 60$ °C.
Physical process: melting of CNN.
Chemical process: thermal hydrolysis according to eqn. (1).

Stage 2

$T = 100$–150 °C.
Physical process: boiling and distillation of the azeotrope HNO_3–H_2O.
Chemical processes: major reaction, shift of the thermal hydrolysis equilibrium according to eqn. (2); minor reaction, oxidation of Cr^{3+} by means of boiling HNO_3 according to eqns. (3) and (4).

Stage 3

$T = 160\,^\circ$C.
Physical process: melting of intermediates.
Chemical processes: major reaction, oxidation of Cr^{3+} by the decomposition of $Cr(OH)_2NO_3$ according to eqn. (5): minor reaction, displacement of HNO_3 from the basic nitrates by basic bichromate according to eqn. (6).

Stage 4

$T = 170$–$300\,^\circ$C.
Chemical processes: major reactions, aerial oxidation of basic chromium chromates to normal chromate according to eqns. (8) and (9); minor reaction, displacement of HNO_3 from basic nitrates by basic chromate according to eqn. (7).

Stage 5

$T = 300$–$420\,^\circ$C.
Chemical process: thermal decomposition of normal chromium chromate to Cr_2O_3 according to eqns. (10) or (11) and (12).

Stage 6

$T = 420\,^\circ$C.
Physical process: formation of crystalline α-Cr_2O_3 from the amorphous product of reactions (10) or (11) and (12).

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