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A reinvestigation of the thermal decomposition products of $(NH_4)_2CrO_4$ and $(NH_4)_2Cr_2O_7$

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Abstract

Various intermediates have been proposed to form during the thermal decomposition of $(NH_4)_2CrO_4$ and $(NH_4)_2Cr_2O_7$ to Cr_2O_3. These high-temperature reactions were examined again by means of infrared, Raman and electronic spectroscopy as well as X-ray powder diffraction. Ammonium chromate was found to decompose to ammonium dichromate in the first step. When ammonium dichromate is heated rapidly up to relatively low temperatures (498–503 K) the main product of an explosive reaction is Cr_2O_3 with some NO_2^- and NH_3 trapped in the solid. With gradual heating of ammonium dichromate, even up to 693 K, the reaction is not a violent one. Instead, the colour of the reactant changes from orange to red, to brown and finally to black. Cr_2O_3 is formed once again with NO_2^- and NH_3 as surface species. The existence of either a CrO_3–NH_3 or a Cr–NH_3 complex is possible after gradual heating of $(NH_4)_2Cr_2O_7$ up to 613 K.

1. Introduction

The protective films formed on steel from a solution of $(NH_4)_2CrO_4$ at various temperatures have been found to be related to an increase in the concentration of chromium in the films obtained at higher temperatures [1]. This can be directly related to the thermal decomposition of ammonium chromate to ammonium dichromate and eventually to Cr_2O_3.

Various authors have already studied the decomposition of $(NH_4)_2CrO_4$ as a precursor to the decomposition of $(NH_4)_2Cr_2O_7$ by means of thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential thermogravity (DTG), X-ray diffraction, mass spectrometry and microscopic methods [2–4]. The kinetics of this first decomposition step have been determined from the variation of pressure of evolving NH_3 as a function of time [4], and by Raman spectroscopy [5]. The thermal decomposition of $(NH_4)_2Cr_2O_7$ is generally represented by the following simplified reaction [2]:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{\Delta} Cr_2O_3(s) + 4H_2O(g) + N_2(g) \qquad (1)$$

This reaction has also been studied before but the conclusions of the authors [3, 6–12] were often controversial and contradictory, especially concerning the large variety of intermediate species which have been proposed.

Mahieu *et al.* [6] proposed the formation of Cr_2O_5, $(CrO_2)_6H_2O$ and CrO_2 at various temperatures before the final product, Cr_2O_3 is obtained.

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This was concluded after, amongst others methods, DTA, TGA, X-ray diffraction, gas chromatography and magnetic susceptibility measurements of the samples. Radioactive tracer techniques were used to determine the oxidation states at different stages of the reaction, and the composition of 39% Cr(III), 61% Cr(VI) after the first stage was interpreted as the presence of Cr(V), while 66% Cr(III), 34% Cr(VI) after the second and third stages was interpreted as the presence of Cr(IV). Cr_2O_5 is, however, generally regarded as $CrO_3 \cdot CrO_2$ [13] and one would thus expect a combination of oxidation numbers VI and IV to occur in the presence of such a compound. Simpson *et al.* [7] also proposed Cr_2O_5 as a possible intermediate, as well as a compound consisting of chains of alternating chromium and oxygen atoms to which NO_2^-, NO_3^{2-} or NH_2 groups are linked. Ill-Huyn Park [2, 3] found by means of TG, DTA, DTG, X-ray diffraction and mass spectrometry that $(NH_4)_2Cr_2O_7$ decomposes to CrO_3 followed by a CrO_3/Cr_2O_3 combination and finally pure Cr_2O_3.

Galwey *et al.* [11] examined decomposed crystals of $(NH_4)_2Cr_2O_7$ by means of an electron microscope and found evidence that the reaction proceeds through the intervention of a melt. The darkening of the dichromate during decomposition was ascribed to dissociative loss of ammonia and the ultimate yielding of CrO_3 as a possible molten intermediate since the melting point of CrO_3 (around 468 K) is towards the lower end of temperatures used during the study. The following reaction was proposed as an initial reaction in the decomposition:

$$(NH_4)_2Cr_2O_7(s) \rightleftharpoons 2CrO_3(s) + 2NH_3(g) + H_2O(g) \qquad (2)$$

Oxidation of NH_3 or NH_4^+ yielding N_2 and N_2O as gaseous products was suggested to follow this reaction, and the internal structure of the solid product closely resembled that of the product obtained in the reaction of CrO_3 with roughly 20% $(NH_4)_2CO_3$ at 513 K.

Results obtained during an infrared and X-ray diffraction study by Zaki and Fahim [12] showed, in contrast to results obtained by other authors, that the product after the first stage of the decomposition of $(NH_4)_2Cr_2O_7$ consists mainly of a highly distorted Cr_2O_3 compound together with small amounts of CrO_3. From infrared results it was concluded that NH_4^+ and H_2O were present as surface species. These authors also found that although weight loss in the second step of the reaction indicated the formation of CrO_2, X-ray diffraction results revealed the domination of a still highly strained Cr_2O_3 species at the expense of the CrO_3 species. No trace was found of CrO_2. The final product was highly stoichiometric α-Cr_2O_3.

2. Experimental details

All samples of $(NH_4)_2CrO_4$ and $(NH_4)_2Cr_2O_7$ were of analytical grade and were reacted in air in an open system. $(NH_4)_2CrO_4$ was decomposed at 393 K for various periods of time up to 48 h. $(NH_4)_2Cr_2O_7$ was heated rapidly up to relatively low temperatures, (1) 473, (2) 498, and (3) 503 K, and gradually up to (1) 518 and (2) 613 K. The last sample was gradually heated up to 693 K and this temperature was maintained on the sample for 3 h.

Infrared spectra of the products were recorded on the Bruker IFS 113 v FT-IR spectrometer with a resolution of 2 cm^{-1}. Electronic diffuse reflectance spectra were recorded on a Beckman DU-2 spectrophotometer. The Raman measurements were made on a Z-24 Dilor Raman spectrometer using an He–Ne laser to excite the spectra. A high-temperature cell obtained from Dilor in Lille, France, was used for high-temperature measurements.

3. Results and discussion

3.1. *Ammonium chromate*

It has previously been shown that ammonium chromate decomposes to ammonium dichromate in a single step [5]. Raman spectra recorded here up to 393 K also showed the formation of only ammonium dichromate up to this temperature. Although the decomposition of ammonium chromate and ammonium dichromate proceeds even at room temperature [2], traces of the reactant were still present after 48 h at 393 K. This was confirmed by X-ray powder diffraction patterns and diffuse reflectance electronic spectra of ammonium chromate, its decomposition products and ammonium dichromate. The positions of absorption maxima in the electronic spectra (Fig. 1) of these compounds are shown in Table 1. The 340 nm band in $(NH_4)_2CrO_4$ has been assigned to the low energy $^1T_2$ state $(1t_1 \ldots 2e)$ and the dipole forbidden $^1T_1$ by analogy with permanganate [14]. Subsequent decomposition of $(NH_4)_2CrO_4$ coincides with the decomposition of $(NH_4)_2Cr_2O_7$.

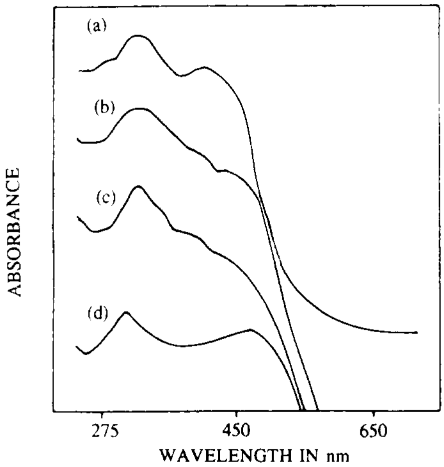

Fig. 1. Diffuse reflectance electronic spectra of: (a) $(NH_4)_2CrO_4$; (b) $(NH_4)_2CrO_4$ after 18 h at 393 K; (c) $(NH_4)_2CrO_4$ after 48 h at 393 K; (d) $(NH_4)_2Cr_2O_7$.

TABLE 1

Positions of the absorption band maxima (in nanometres) in the diffuse reflectance electronic spectra of $(NH_4)_2CrO_4$ and some of its decomposition products

$(NH_4)_2CrO_4$	Products at 393 K		$(NH_4)_2Cr_2O_7$
	18 h	48 h	
340	340	335	330
415	415	415	–
–	455	455	455

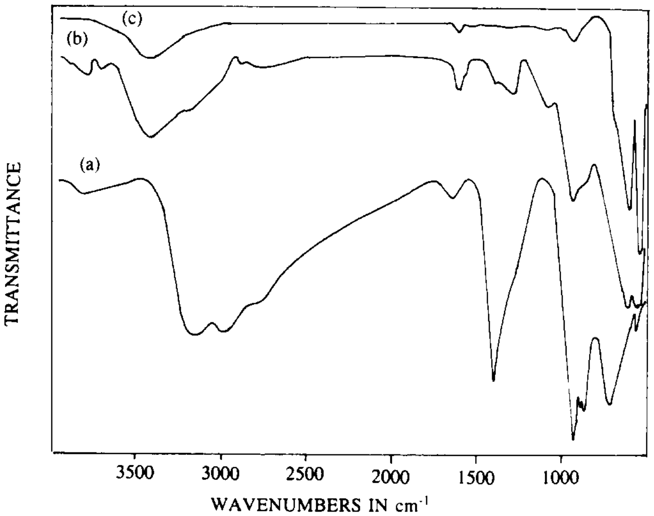

Fig. 2. Infrared spectra of: (a) $(NH_4)_2Cr_2O_7$ and its decomposition products; (b) at 498 K; (c) at 503 K.

3.2. *Ammonium dichromate*

Raman spectra recorded during decomposition showed that only ammonium dichromate exists up to 473 K. At higher temperatures the decomposition products were black in colour so Raman spectra could not be obtained, and further decomposition was investigated by means of infrared spectroscopy.

3.3. *Infrared spectra*

The mid-infrared spectra of $(NH_4)_2Cr_2O_7$ and its products at two different states of decomposition with rapid heating up to relatively low temperatures (498 and 503 K) are shown in Fig. 2, with spectra of those decomposition products obtained after gradual heating at two higher temperatures, 518 and 613 K, compared with the spectra of CrO_3 and Cr_2O_3 in Fig. 3. The infrared-active modes which were observed for the various products are compared

TABLE 2

Infrared bands of some decomposition products of $(NH_4)_2Cr_2O_7$ (ADC) compared with CrO_3, Cr_2O_3 and the chromium–ammonia complex $[Cr(NH_3)_6]Cl$ ($CrNH_3$ compl). All frequencies are in cm^{-1}

ADC	High-temperature products					$CrNH_3$ complex	CrO_3	Cr_2O_3
	498 K	503 K	518 K	613 K	693 K			
3128	3421	3431	3151	3432	3446	3330	–	–
1633	1628	1646	1670	–	–	1622	1618	–
–	–	–	1646	–	–	–	–	–
1402	–	–	1387	–	–	1334	–	–
–	1276	–	1277	–	–	–	–	–
–	–	–	–	1120	–	1120	–	–
–	–	–	–	958	–	–	959	–
949	947	–	–	949	–	–	944	–
–	–	–	–	–	–	–	907	–
898	–	–	899	–	–	–	–	–
724	–	–	745	–	–	–	–	–
–	621	–	–	616	618	–	–	623
–	561	–	557	568	558	–	–	558
–	–	–	–	492	–	492	–	–
–	–	460	–	–	445	–	–	–
–	–	–	–	470	412	474	–	–
–	–	–	–	461	–	459	–	–
–	–	444	–	–	–	–	–	444
–	–	411	–	–	–	–	–	415
–	–	325	–	–	–	325	–	–
–	–	–	–	–	307	–	–	307

with those of pure $(NH_4)_2Cr_2O_7$, CrO_3, Cr_2O_3 and the complex $[Cr(NH_3)_6]Cl_3$ in Table 2.

3.3.1. Rapid heating up to 498 K

As was expected, a violent reaction yielded a black and green solid. Infrared spectra (Fig. 2) showed a lower intensity for the ammonium bands, with the appearance of ammonia bands at 3421 and 1628 cm^{-1}. A weak band at 1276 cm^{-1} can possibly be attributed to NO_2^- groups trapped in the solid during decomposition as the infrared spectrum of $[Cr(NH_3)_5NO_3](NO_2)_2$ has a band at 1277 cm^{-1} [7] which is absent for other chromium complexes containing only NH_3, H_2O and NO_3^{2-} groups. There is a decrease in the intensity of the characteristic dichromate bands between 947 and 724 cm^{-1}, while the bands appearing at 621 and 561 cm^{-1} are characteristic of Cr_2O_3.

3.3.2. Rapid heating up to 503 K

For this product, NH_3 bands [15] are observed at 3431 and 1626 cm^{-1} with no sign of NH_4^+ bands. In the far-infrared spectrum a band at 460 cm^{-1} in the spectra of both $(NH_4)_2Cr_2O_7$ and its decomposition product at

498 K were absent here, but the two new bands appear at 444 and 411 cm^{-1} which were also observed in the far-infrared spectrum of Cr_2O_3.

3.3.3. Gradual heating up to 518 K

Gradual heating resulted in a slower reaction so that no violent reaction was visible. The product was a black solid. In the infrared spectrum of this product (Fig. 3) the ammonium bands are of a lower intensity than those occurring from 3128 and 1402 cm^{-1} in the spectrum of untreated $(NH_4)_2Cr_2O_7$ and these bands have shifted to 3151 and 1387 cm^{-1} respectively. A shoulder at around 3400 cm^{-1} and a new band at 1646 cm^{-1} indicate the formation of NH_3 [16], while the band at 1277 cm^{-1} can again be ascribed to NO_2^- [7] formation. Dichromate bands are still present between 950 and 880 cm^{-1} but the band at 724 cm^{-1} has shifted to 745 cm^{-1}. The broad band at 557 cm^{-1} appears to be the band characteristic of Cr_2O_3.

3.3.4. Gradual heating up to 613 K

The presence of NH_3 in this product is indicated by the band at 3432 cm^{-1} (Fig. 3). A broad band, split into two modes at 568 and 616 cm^{-1},

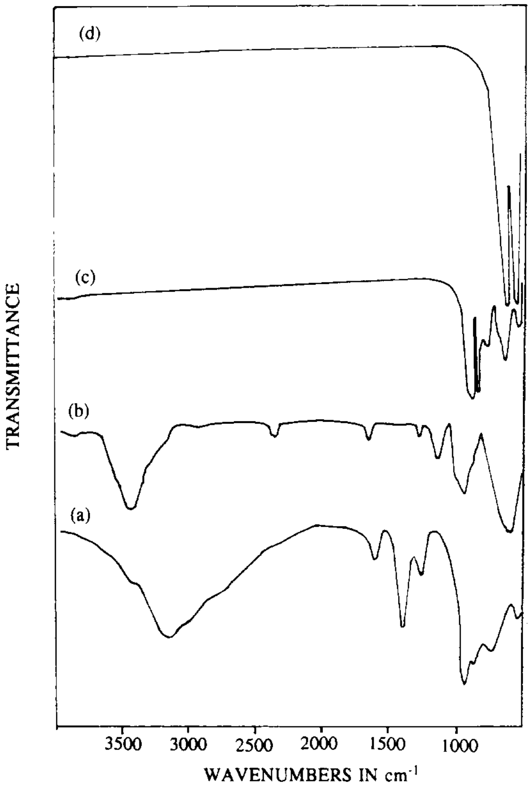

Fig. 3. Infrared spectra of: (a) $(NH_4)_2Cr_2O_7$ after treatment at 518 K; (b) $(NH_4)_2Cr_2O_7$ after treatment at 613 K; (c) CrO_3; (d) Cr_2O_3.

indicates the existence of Cr_2O_3. A small amount of CrO_3 could also be present, as is indicated by the presence of the low-intensity bands at 958 and 949 cm^{-1}. Nakamoto [15] reported a spectrum of a Cr(III) complex, $[Cr(NH_3)_6]Cl_3$. The far-infrared bands of the product obtained at 613 K, which occur at 492, 470 and 461 cm^{-1}, are in concurrence with ν(Cr–N) bands reported at 492, 474 and 459 cm^{-1}. The low-intensity band at about 1120 cm^{-1} is present in both the spectrum of the product recorded here and that of the Cr(III) complex reported by Nakamoto [15].

3.3.5. *Product after 3 h at 693 K*

Strong, sharp bands characteristic of Cr_2O_3 were observed for this product at 618 and 558 cm^{-1} in the mid-infrared and at 445, 412 and 307 cm^{-1} in the far-infrared region. NH_3 bands of a very low intensity were still visible at 3446 cm^{-1}.

3.4. *Diffuse reflectance spectra*

Diffuse reflectance electronic spectra of $(NH_4)_2Cr_2O_7$ and some of its decomposition products, as well as CrO_3 and Cr_2O_3, are shown in Fig. 4 with the absorption maxima in Table 3.

The diffuse reflectance spectra of CrO_3 and Cr_2O_3 have been reported before without assignments [17]. By comparison of the maxima in the spectra only ammonium dichromate is present in the samples heated up to 423 and 473 K, and samples decomposed above 493 K consisted of Cr_2O_3 only. Traces of CrO_3 could be present in the sample decomposed at 613 K as a low-intensity absorption band of this sample at 525 nm coincides with a band in the electronic spectrum of CrO_3.

4. Conclusions

At temperatures up to 393 K in air in an open system $(NH_4)_2CrO_4$ decomposes to $(NH_4)_2Cr_2O_7$ only, and this occurs in a single step. Further decomposition steps coincide with the decomposition of $(NH_4)_2Cr_2O_7$.

With a complex process and a large variety of intermediate species being proposed by various authors, conclusions regarding the decomposition of $(NH_4)_2Cr_2O_7$ were often ambiguous. Of the intermediates that have been proposed the formation of Cr_2O_5, $(CrO_2)_6H_2O$ and CrO_2 seems unlikely. Infrared and Raman spectra were not included as methods of identification in the previous studies to confirm the existence of such intermediates. No evidence of the formation of such a compound was found during this study.

Only $(NH_4)_2Cr_2O_7$ exists up to 473 K, as was confirmed by the Raman spectra recorded up to this temperature. Rapid heating of the dichromate above 493 K results in a violent decomposition reaction, yielding a black and green solid. The main product is Cr_2O_3. According to infrared spectra relatively few ammonium groups are present after heating rapidly up to 498 K, with no sign of these groups after such a reaction at 503 K. Instead NH_3

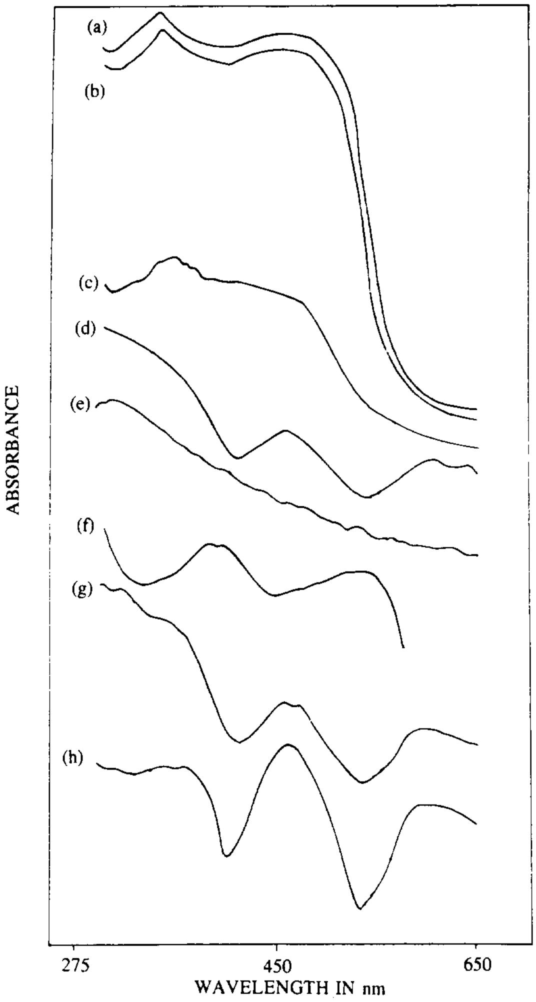

Fig. 4. Diffuse reflectance electronic spectra of $(NH_4)_2Cr_2O_7$: (a) untreated; (b) after heating to 423 K; (c) to 473 K; (d) to 493 K; (e) to 613 K; (f) compared with that of CrO_3; (g) $(NH_4)_2Cr_2O_7$ after treatment at 773 K; (h) Cr_2O_3.

and even traces of NO_2^- groups, presumably trapped in the solid, are observed.

When $(NH_4)_2Cr_2O_7$ is heated gradually the subsequent reaction is not a violent one, even if the temperature is raised up to 613 K. Instead the orange crystals change to a dark red, then brown and finally a black colour. Ammonium bands in the infrared spectra shifted to lower wavenumbers, probably an indication that the groups are more free to rotate than before. When $(NH_4)_2Cr_2O_7$ is heated gradually so that no violent reaction takes place, traces of CrO_3 are likely to occur in the product as part of a CrO_3–Cr_2O_3 mixture because of a side reaction taking place in an open system. Such a

TABLE 3

Positions of the absorption band maxima (in nm) in the diffuse reflectance electronic spectra of various decomposition products of $(NH_4)_2Cr_2O_7$ (ADC)

ADC	Products of ADC					CrO_3	Cr_2O_3
	423 K	473 K	493 K	613 K	773 K		
330	335	340	325	280	280	–	280
–	–	–	360	360	335	–	345
–	–	–	–	400	360	375	360
455	455	455	460	460	460	–	460
–	–	–	600	525	600	525	600

reaction was proposed by Galwey *et al.* [11] as an initial main reaction in the decomposition (reaction (2)).

Galwey [11] suggested that the reaction could be reversible. Evidence of the existence of small amounts of CrO_3 in the decomposition products was found here by means of Fourier transform (FT) IR and diffuse reflectance electronic spectra in the product obtained at 613 K with Cr_2O_3 as the main product. The reversibility of the reaction has also been investigated [11] by treating solid CrO_3 with various solutions, *e.g.* NH_3, $(NH_4)_2CO_3$ and NH_4NO_3. This yielded orange crystals in each case, identified by means of FT IR as $(NH_4)_2Cr_2O_7$ leading to the conlusion that reaction (2) is indeed reversible. The existence of CrO_3 and Cr_2O_3 in one product could result in a black colour because of mixed valence oxides: Cr(VI) in CrO_3 and Cr(III) in Cr_2O_3.

NO_2^- and NH_3 detected in decomposition products obtained at 498, 518 K and 498, 503, 518, 613 and 693 K respectively are probably present as surface species. The bands in the infrared spectrum of the decomposition product obtained at 613 K coincide with that of ν(Cr–N) in the spectrum of the $[Cr(NH_3)_6]Cl_3$ complex indicating the possible existence of a CrO_3–NH_3 or a Cr–NH_3 complex. The final product in the decomposition of $(NH_4)_2Cr_2O_7$ is the most stable oxide of chromium, α-Cr_2O_3.

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