

THERMOGRAVIMETRIC AND EPR STUDY
OF THE VACUUM THERMAL DECOMPOSITION OF SOME ZINC
AND COPPER(II) CHROMATES

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The thermal decompositions in vacuum of the compounds ZnCrO_3 , $\text{ZnCrO}_4 \cdot 3.5 \text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ and CuCrO_4 have been investigated using a combination of various techniques: TG, EPR, IR and X-ray.

While the TG and X-ray data confirm the final formation of Cu(I) and Zn chromites with the spinel structure resulting from the spontaneous thermal reduction of the Cr(VI) ions, EPR reveals the progressive formation and decay of the following intermediate paramagnetic species: Cr(V) ions and Cr(III) species either dispersed in the M(II) oxide bulk and/or clustered in a Cr_2O_3 -like phase, or finally ordered in the chromite phase formed at high temperature.

The paramagnetic species which appear, as well as their temperature ranges of stability, are strongly dependent on the nature of the M(II) ion and the Cr(III)/M(II) ratio.

The successive detection of these intermediates by EPR yields some detailed information about the decomposition mechanisms of the chromates.

We have shown recently that combining various physical techniques such as electron paramagnetic resonance (EPR), thermogravimetry (TG), X-ray diffraction (XR) and IR spectroscopy can prove useful for a complete elucidation of complex decomposition processes for some inorganic oxy salts such as oxalates [1, 4, 5], chromates [2, 3] or thiosulfates [6–8]. Our previous work concerning the examination of solid-state reactions between alkaline-earth chromates and oxalates is most interestingly extended to the investigation of the corresponding copper and zinc systems, because of the well-known catalytic properties of copper chromite [9, 20], zinc chromite [10b, 18] and various mixed Cu–Cr–Zn oxides [10a, 10c, 20].

Owing to the fact that all these compounds can appear either as intermediates or as end-products during the thermal analysis of the corresponding pure chromates or oxalates their mixture and/or their solid solutions, it is of critical importance to elucidate their thermal decomposition mechanisms.

The present contribution deals with the investigation of all the successive and interrelated steps occurring during thermal analysis of normal and basic zinc chromate and of copper(II) chromate. In particular, EPR is combined with TG, XR and IR for the identification of all the intermediate species containing paramagnetic ions (Cr(V), Cr(III), Cu(II)) and for the explanation of their structural interrelations.

Experimental

Starting materials

ZnCrO₄ was prepared hydrothermally as suggested by Clark and Reinhardt [12], from 4.5 g ZnCO₃·Zn(OH)₂ (zinc hydroxide carbonate) Merck, pure, 5 g CrO₃ (Merck, p.a.), and 5 ml H₂O. The temperature was progressively raised (6 hr) from 20 to 200–210° and the bomb (or sealed tube) kept at that temperature for about 16 hr. It was then progressively (2 hr) cooled down to room temperature. The product was filtered, washed with cold water and dried overnight at 110°.

ZnCrO₄ · 3.5 Zn(OH)₂ · H₂O was prepared by mixing at room temperature equimolar solutions of ZnCl₂ and K₂CrO₄ (Merck, p.a.). The yellow precipitate was filtered off, washed thoroughly with cold water and dried overnight at 70°.

CuCrO₄ was synthesized in a way similar to the Zn compound: 4 g CuCO₃ · Cu(OH)₂ (Merck, pure) was added to 6.5 ml H₂O at room temperature. 7.2 g CrO₃ was progressively added while gently heating to remove and evolve CO₂. The mixture was then poured into the hydrothermal bomb and left at 220° for about 14 hr. The resulting red-brown precipitate was filtered off, washed with cold water and dried overnight at 100°.

The purities of the normal chromates were checked by chemical analysis: Zn by complexometric titration, Cu by electrolysis and CrO₄²⁻ by iodometry. Moreover, the X-ray diagrams and the IR spectrum of CuCrO₄ were identical to those reported in the literature [13]. The proposed formula for the basic Zn-chromate, as resulting from chemical analysis (Zn and CrO₄²⁻) and TG analysis (OH and H₂O), does not correspond to any of the numerous basic chromates referred to in the literature [14, 15]. The new compound corresponds best to the III-β phase of Feitknecht and Hugli-Carmes [16], as checked by X-ray diffraction.

Thermal analysis

The decomposition was investigated by TG in dynamic vacuum (2.10⁻³ torr) in the temperature range 25–800°, the curves being recorded on a TH-59 Adamel thermobalance using a heating rate of 150° h⁻¹.

EPR

The EPR measurements were carried out using an X-band (9.56 GHz) Varian E-12 spectrometer with a 100 kHz field modulation. The samples were heated in dynamic vacuum (2.10⁻³ torr) for every 25 degrees of temperature from room temperature up to 900°. After a 30 min heating, the decomposition was interrupted by cooling the tube to 20°, and the EPR spectrum was then recorded in vacuum at either 77 or 300 K. The *g* factors were evaluated by comparison to the *g* value of the DPPH radical (*g* = 2.0036) used as reference.

IR spectra

Infrared spectra (4000–200 cm⁻¹) were recorded on KBr disks using a Beckman IR-12 spectrometer.

X-ray diffraction

X-ray diffraction patterns were obtained using a CGR diffractometer and Cu-K_α radiation.

Results and discussion

ZnCrO₄

The thermal decomposition of ZnCrO₄ in vacuum proceeds in a single step as revealed by the TG technique: some oxygen is released already from 300° up, but

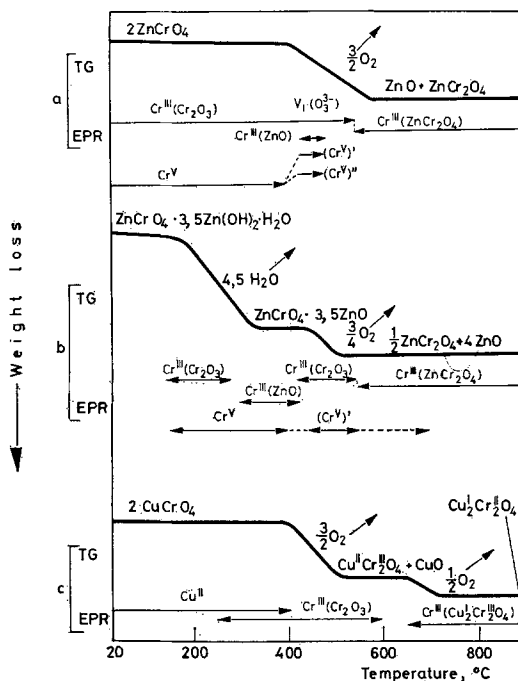
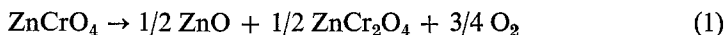


Fig. 1. TG and EPR data for the vacuum thermal decomposition of a) ZnCrO₄; b) ZnCrO₄ · 3.5 Zn(OH)₂ · H₂O; c) CuCrO₄; EPR signals as indicated

the main weight loss is observed between 400 and 600° (Fig. 1a). The total loss corresponds to the release of 3/4 moles of oxygen, according to the scheme [12]



X-ray and IR analyses of the final residue formed at 800° confirm the presence of ZnCr₂O₄ and ZnO.

The use of EPR permits the identification of some important intermediate steps in the reduction process of chromium (VI): three Cr(III) species (signals A, A' and B), three Cr(V) species (signals C, C' and C'') and the V₁ (O₃²⁻) radical (signal D)

Table 1
EPR signals observed during thermal analysis of zinc chromate,
and their assignments

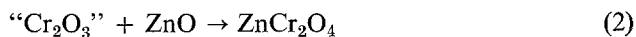
Signals	T range, °C	Linewidth, gauss	<i>g</i> factors	Assignments
<i>A</i> ↓ <i>A'</i>	RT → 520 ↓ 900	300 → 1120 ↓ 470	$g_{\text{iso}} \simeq 1.975$ $g_{\text{iso}} = 1.979 \rightarrow 1.979$	Cr(III)/Cr ₂ O ₃ Cr(III)/ZnCr ₂ O ₄
<i>C</i> <i>C'</i> <i>C''</i>	RT ↓ 400	→ asymmetric →	→ $g_{\perp} = 1.9804$ $g_{\parallel} = 1.9510$) $g_{\text{iso}} = 1.9698$ → $g_{\perp} = 1.9817$ $g_{\parallel} = 1.9476$) $g_{\text{iso}} = 1.9691$	Cr(V)
	440 → 480	asymmetric	$g_{\perp} = 1.9817$ $g_{\parallel} = 1.9352$) $g_{\text{iso}} = 1.9662$	(Cr(V))'
			$g_{\perp} = 1.9792$ $g_{\parallel} = 1.9450$) $g_{\text{iso}} = 1.9678$	(Cr(V))''
<i>B</i>	440 → 480	asymmetric	$g_{\perp} = 1.9894$ $g_{\parallel} = 1.9653$) $g_{\text{iso}} = 1.9813$	Cr(III)/ZnO
<i>D</i>	480	—	$g_{\text{iso}} = 2.077$	V _I = O ₃ ²⁻

are successively and/or simultaneously detected. Their characteristics (temperature ranges of stability, *g* values, linewidths) are listed in Table 1.

The starting material exhibits two EPR signals when degassed at room temperature; these can be attributed unambiguously to Cr(III) ions incorporated in a Cr₂O₃-like phase (signal *A*) and to Cr(V) ions (signal *C*) (Fig. 2a).

The shape of signal *A* does not change much as a function of temperature, except between 400 and 550°, where its linewidth increases to a large extent (Figs 2b and 2c). This means that in the "Cr₂O₃" formed, the Cr(III)-Cr(III) interaction becomes more and more important as the reduction degree Cr(VI) → Cr(III) increases. The latter becomes predominant above 400°.

From 550–600° up, the linewidth drastically decreases again (Fig. 3), and at 700° a linewidth of nearly 600 gauss already characterizes the formation of a chromite phase. The linewidth decrease from 1050 to ~500 gauss clearly illustrates a migration of the Cr(III) ions from a compact Cr₂O₃-like cluster to the well-ordered zinc chromite phase. The reaction



should effectively occur in this range of temperature [23, 24]. It is noteworthy that the g_{iso} factor of the Cr(III)/Cr₂O₃ species remains constant (1.975–1.980) as a

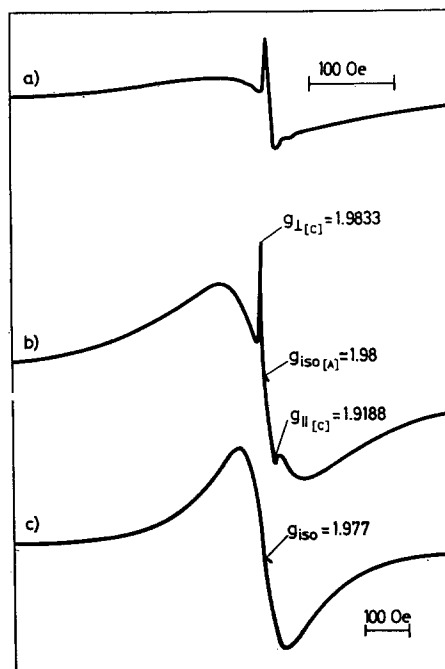


Fig. 2. EPR spectra of ZnCrO_4 after vacuum activation a) at room temperature; b) at 335° ; c) at 480°

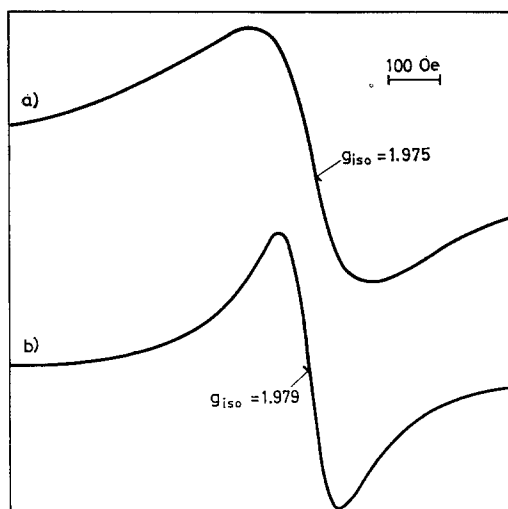


Fig. 3. EPR spectra of ZnCrO_4 after vacuum activation a) at 600° (signal A); b) at 850° (signal A')

function of temperature. Such values could characterize a Cr(III)-rich compound. A pure bulk Cr_2O_3 phase always characterized by a g factor of 2.20–2.30 is never formed during the calcination process.

In the range 25–400°, the g factor of signal C (Cr(V)) changes a little (Table 1), indicating that the surface and/or the bulk geometry of the Cr(V) ions undergoes some rearrangement. Moreover, between 400 and 480°, signal C is highly perturbed and gives rise to two other similarly-shaped and nearly superimposed signals (C' and C''), which nevertheless can easily be resolved and characterized (Table 1). They still belong to some Cr(V) species, which are rapidly formed when the beginning of the oxygen release is detected by TG, and disappear at 480° when the reduction rate is the most important, as seen from the TG curve (i.e. when Cr(III) is formed).

Another asymmetric and very narrow EPR signal (B) is detected in this critical range of temperature (440–480°); it is attributed to Cr(III) ions dissolved in the ZnO lattice, freshly generated at this temperature [17]. ZnO formation is also evidenced by the presence at 480° of the V_1 radical (O_3^{3-} adsorbed species), which gives rise to a weak but characteristic EPR signal (signal D – Fig. 2c). The formation of O_3^{3-} on the ZnO surface has previously been observed and the mechanism discussed [5].

Above 480°, both Cr(III)/ZnO and O_3^{3-} species disappear, confirming the X-ray and IR investigations of the solid residue at about 500°: most of the ZnO has disappeared and ZnCr_2O_4 begins to form. The whole scheme is summarized in Table 2. $\text{ZnCrO}_4 \cdot 3.5\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$

The TG shows that the thermal decomposition of $\text{ZnCrO}_4 \cdot 3.5\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ proceeds in two distinct steps:

a) Dehydration between 175 and 330°:

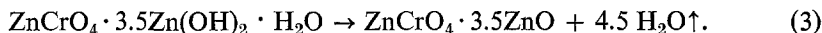
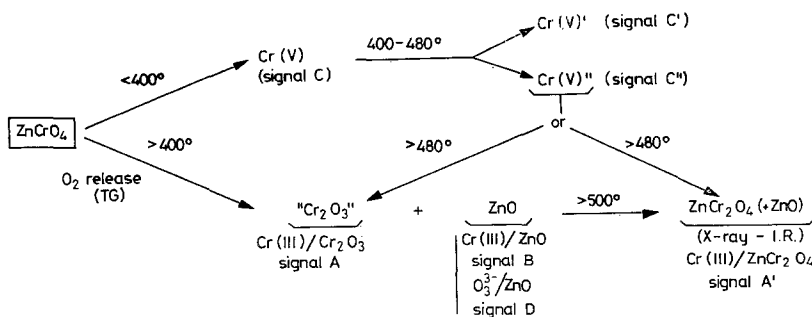
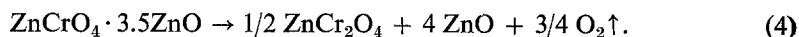


Table 2

Intermediate phases formed during the vacuum thermal decomposition of CuCrO_4 , as evidenced by TG, EPR, IR and XR.



b) Decomposition between 440 and 550°:



X-ray diffraction and IR analyses confirm the composition of the final residue at 700°: ZnCr_2O_4 (spinel) + ZnO .

The thermal decomposition of another basic zinc chromate, $\text{ZnCrO}_4 \cdot 3-4\text{Zn}(\text{OH})_2$ (the well-known III- β Feitknecht phase [16]), has been studied earlier by the combined X-ray, TG/DTA techniques [18]. An intermediate stable phase is also obtained after dehydration and the authors conclude that it should be zinc dichromate. We have also examined the intermediate chromate(VI) phase resulting from the dehydration of $\text{ZnCrO}_4 \cdot 3.5\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (plateau between 330 and 440°) and the possibility of dichromate ion formation has been questioned. The residue obtained at 400° is amorphous as concluded from X-rays. However, the IR spectrum, which closely resembles that of the starting material, confirms that CrO_4^{2-} ions are still present: typical absorption peaks near 920–940, 780 and 400 cm^{-1} could be assigned, respectively to the $\nu_{\text{sym}}(\text{Cr}^{\text{VI}} - \text{O})$ and $\gamma_{\text{as}}(\text{Cr}^{\text{VI}} - \text{O})$ and $\delta(\text{O} - \text{Cr}^{\text{VI}} - \text{O})$ modes belonging to a CrO_4 vibrating entity [19].

No typical $\text{Cr}_2\text{O}_7^{2-}$ absorption patterns could be observed [19].

The decomposition process was examined more closely by EPR. The same paramagnetic Cr(V) and Cr(III) ions are detected as during the decomposition of ZnCrO_4 , but they appear and disappear here at quite different calcination temperatures. The two decomposition processes are compared in Fig. 1a and 1b. The corresponding EPR parameters are listed in Table 3.

Table 3

EPR signals observed during the thermolysis of $\text{ZnCrO}_4 \cdot 3.5\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$, and their interpretation

Signal	T range, °C	Linewidth, gauss	<i>g</i> factors	Assignment
A (weak)	150–275	~400?) could not be measured ↓ $g_{\text{iso}} = 1.977-1.978$	Cr(III)/ Cr_2O_3
A disappears	275–425	800		Cr(III)/ Cr_2O_3
A (strong)	425–550 ↓ 900	400		Cr(III)/ ZnCr_2O_4
B	300–400/425	—	—	Cr(III)/ ZnO
C	150–400	—	($g_{\perp} = 1.9817 \rightarrow 1.9835$ $g_{\parallel} = 1.9495 \rightarrow 1.9480$ $g_{\text{iso}} = 1.9710 \rightarrow 1.9718$)	Cr(V)
↓ C'	465–550 (traces up to 700)	—		($g_{\perp} = 1.9832 \rightarrow 1.9833$ $g_{\parallel} = 1.9148 \rightarrow 1.9188$ $g_{\text{iso}} = 1.9604 \rightarrow 1.9621$)

Small amounts of Cr(III) ions belonging to a Cr_2O_3 -like phase (signal *A*), as well as some Cr(V) species, appear above 150° . This suggests that some reduction occurs during the dehydration process, possibly *via* surface reducing OH^- ions. Above 275° , the Cr(III)/ Cr_2O_3 species surprisingly disappear, but at 300° some Cr(III) ions are incorporated in the ZnO lattice as evidenced by the characteristic but still rather weak EPR signal (signal *B*). This is explained if we consider that the amount

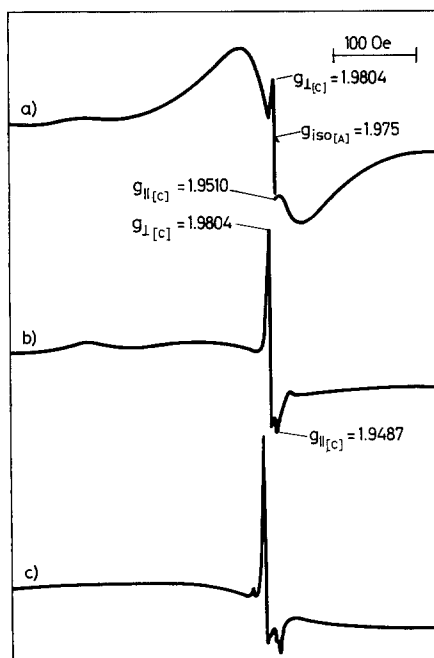
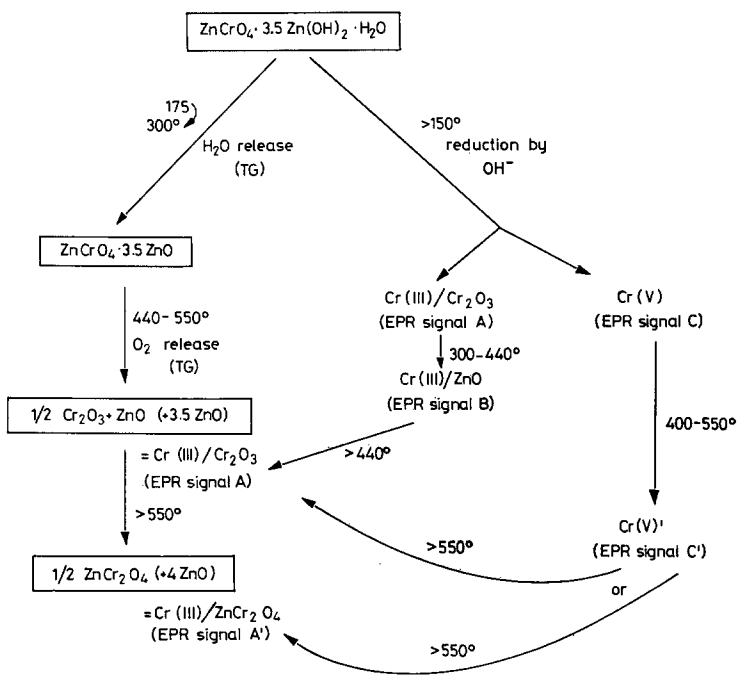


Fig. 4. EPR spectra of $\text{ZnCrO}_4 \cdot 3.5 \text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ after vacuum activation a) at 225° ; b) at 550° ; c) at 800°

of ZnO stemming from the Zn(OH)_2 dehydration is sufficient to dissolve all the Cr(III) which has been preliminarily formed. It must be stressed that in the case of thermal analysis of ZnCrO_4 the same signal appears at 440° , a temperature at which ZnO begins to appear. This shows that signal *B* must be related to the formation of ZnO, and confirms its assignment to the Cr(III)/ZnO species. At 400° , the TG shows some oxygen release, but the Cr(VI) reduction becomes important only from 450° up. Above this temperature a very strong EPR signal, similar to *A*, reappears, indicating that most of the reduced chromium forms again a Cr_2O_3 -like phase. On the other hand, Cr(V) species, which nearly disappear in the range $400-500^\circ$, also reappear above 450° (signal *C'*). The *g* values are slightly different and their variation with increasing calcination temperature (Table 3) illustrates some progressive modification of the support during thermal treatment. Typical Cr(III) (*A*) and Cr(V) (*C'*) superimposed signals, recorded when the compound is calcined at

Table 4

Intermediate phases formed during the vacuum thermal decomposition of $\text{ZnCrO}_4 \cdot 3.5\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$, as evidenced by TG, EPR, IR and XR



550°, are shown in Fig. 4b. Finally, the linewidth of *A* decreases progressively above 550°, indicating a progressive Cr(III) dissolution into an ordered ZnCr_2O_4 phase (signal *A'*, Fig. 4c). The whole reduction process is summarized in Table 4.

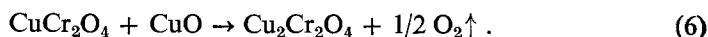
CuCrO_4

The thermal decomposition of CuCrO_4 has been investigated previously by several authors [9a, 20, 24, 25]. Our TG data confirm the well-known two-stage decompositions (Fig. 1c):

between 400 and 505°:



Between 650 and 710°:



It could be seen further that the reaction of Cu(II) chromite with CuO occurs at a slightly lower temperature in vacuum than in air or in N_2 (from 800–850° up) [20, 24, 25]. The residue formed between 550 and 650° has been identified as containing

CuCr_2O_4 by IR and as containing Cr_2O_3 by EPR, which supports that both species are present as suggested by reaction (5). Indeed, the end-product obtained after calcination at 800° has been unambiguously assigned to $\text{Cu}_2\text{Cr}_2\text{O}_4$ by X-ray diffraction [21], EPR [22], and IR spectroscopy [23]. Moreover, X-ray diffraction accounts for the absence of Cu_2O and metallic copper, and the total disappearance of CuCrO_4 , CuCr_2O_4 and Cr_2O_3 , but shows some residual CuO (ca. 2%).

The EPR investigation of the decomposition path reveals some additional interesting features. Three signals are observed: Cu(II) ions in the starting material, Cr(III) ions in Cr_2O_3 clusters, and Cr(III) ions in the final Cu^{I} spinel phase (respectively, signals *E*, *F* and *G* – Table 5 and Fig. 5).

Table 5
EPR signals observed during thermal analysis of CuCrO_4 ,
and their interpretation

Signal	T range, $^\circ\text{C}$	Linewidth, gauss	g_{iso} value	Assignment
<i>E</i>	400	1250	~ 2.15	$\text{Cu(II)}/\text{CuCr}_2\text{O}_4$
<i>F</i>	250–600	1300	~ 2.4	$\text{Cr(III)}/\text{Cr}_2\text{O}_3/ +$ $+ \text{Cu}^{\text{II}}\text{Cr}_2\text{O}_4?$
<i>G</i>	650–900	200	1.982	$\text{Cr(III)}/\text{Cu}_2\text{Cr}_2\text{O}_4$

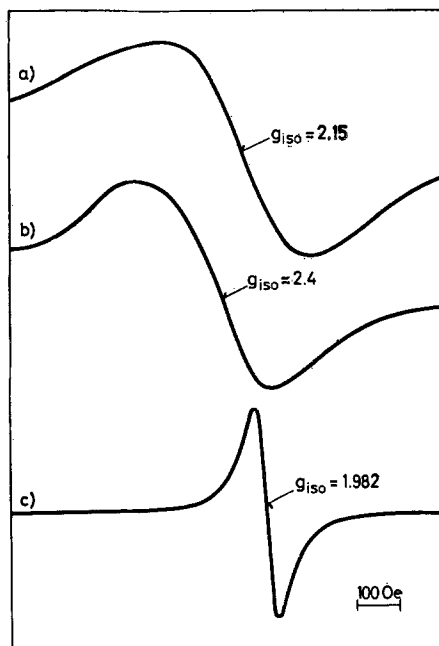
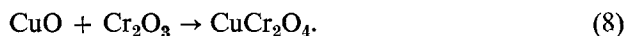
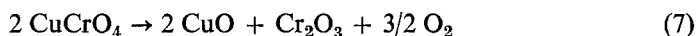


Fig. 5. EPR spectra of CuCrO_4 after vacuum activation a) at room temperature $\text{Cu(II)}/(\text{CuCrO}_4)$; b) at 600° $\text{Cr(III)}/(\text{Cr}_2\text{O}_3)$; c) at 650° $\text{Cr(III)}/(\text{Cu}_2\text{Cr}_2\text{O}_4)$

The starting chromate exhibits only a broad, nearly symmetric, Cu(II) EPR signal. It decreases from 250° up, and between 250 and 400° another very broad signal appears and superimposes itself on the initial Cu(II) signal. The g_{iso} value near 2.4 could characterize some Cr(III), forming a nearly pure Cr₂O₃ bulk phase [22]. The superposition of the two signals reveals that the reduction process occurs earlier (250°) than suggested by the TG alone (400°). From 400° up, only the Cr(III) signal remains. Furthermore, its assignment to Cr₂O₃ can be confirmed by the absence of any EPR signal below the Cr₂O₃ Neel temperature.

It is interesting to point out that while EPR allows the unambiguous detection of Cr₂O₃, it does not yield any definite proof of CuCr₂O₄ formation. Coordinated Cu(II) ions in the latter, as well as in CuO, do not necessarily show an EPR signal. On the other hand, the Cr(III) ions in such a phase are characterized by a g_{iso} value near 1.98 and by a medium or a weak linewidth (less than 1000-800 gauss). Shultz *et al.* [9a] tried to record an EPR spectrum of CuCr₂O₄, but could not observe any signal. In our case, neither a Cr(III)/CuCr₂O₄, nor eventual Cu(II)/CuCr₂O₄, nor any other Cr(V) intermediate species have been detected by EPR. However, no conclusions about their existence can be drawn, as such weak signals may be obscured by the intense broad band due to the Cr₂O₃ phase.

Nevertheless, the formation of CuCr₂O₄ is detected by IR spectroscopy and it confirms the mechanisms previously proposed by Charcosset *et al.* [24].



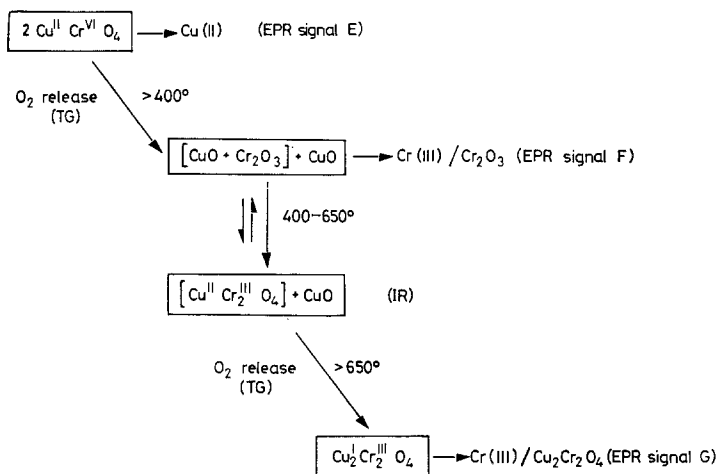
As EPR does detect Cr₂O₃, the copper(II) chromite must be formed mainly by the solid-state reaction between the Cu(II) and Cr(III) oxide (reaction 8). The straight-forward decomposition of CuCrO₄ to CuCr₂O₄ as proposed by Sirina *et al.* [25] is then unlikely.

Above 600°, the linewidth and g_{iso} values of the Cr(III) signal regularly decrease. This is due to a lower Cr(III)–Cr(III) interaction in Cr₂O₃ and could indicate that reaction (8) has nearly come to an end.

Above 650°, the TG curve shows a further oxygen release due to the Cu(II) reduction, and simultaneously the g and ΔH values of signal *F* drastically decrease, giving rise to signal *G* (Table 5) and confirming the Cr(III) incorporation into an ordered Cu₂Cr₂O₄ phase. Furthermore, the EPR spectra of the residue calcined at 900° (signal *F*) and of the pure cuprous chromite prepared separately [21] were found identical on comparison. In conclusion, the decomposition scheme of ZnCrO₄ can be summarized as follows (Table 6).

Table 6

Intermediate phases formed during the vacuum thermal decomposition of CuCrO_4 , as evidenced by TG, EPR, IR and XR



Conclusions

As general conclusions, this work shows that:

- a) The combination of physical techniques in addition to TG, among them IR and EPR, can provide detailed information on thermal decomposition processes of oxy salts.
- b) Cr(V) species, often neglected, can be stabilized even in the presence of high oxidation states of other elements,
- c) Precursors, mainly for Zn, are likely to play some important role in the definition of the final product.

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ZUSAMMENFASSUNG — Die thermische Zersetzung der Verbindungen: ZnCrO_4 , $\text{ZnCrO}_4 \cdot 3.5 \text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ und CuCrO_4 in Vakuum wurde unter Anwendung der Kombination verschiedener Techniken, wie TG, EPR, IR und Röntgen, untersucht.

Während die TG- und Röntgen-Daten die schließlich erfolgende Bildung der Chromite von Cu (I) Zn mit der aus der spontanen thermischen Reduktion der Cr (VI)-Ionen hervorgehenden Spinellstruktur bestätigen, zeigt EPR die progressive Bildung sowie den Zerfall der folgenden intermediären paramagnetischen Species: Cr(V)-Ionen und Cr(III)-Species entweder in der Masse des M (II)-Oxids dispergiert und/oder in einer Cr_2O_3 ähnlichen Phase eingeschlossen oder aber endlich in der bei hoher Temperatur gebildeten Chromitphase geordnet.

Sowohl die auftretenden paramagnetischen Species als auch der Temperaturbereich, in welchem sie stabil sind, hängen stark von der Beschaffenheit des M (II)-Ions und des Verhältnisses Cr(III) (M/II) ab.

Der schrittweise Nachweis dieser Zwischenprodukte durch EPR erbringt einige eingehende Informationen über die Zersetzungsmechanismen der Chromate.

Резюме — Изучено термическое разложение в вакууме соединений ZnCrO_4 , $\text{ZnCrO}_4 \cdot 3.5 \text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ и CuCrO_4 , используя различные комбинированные методы, как например, ТГ, ЭПР, ИК спектроскопию и рентгенографию. Методы ТГ и рентгенографии подтверждают конечное образование хромитов одновалентной меди и цинка со структурой шпинели, образующихся вследствие самопроизвольного термического восстановления ионов Cr(VI). Спектроскопия ЭПР устанавливает возрастающее образование и распад следующих промежуточных частиц ионов: Cr(V) и Cr(III), диспергированных в объёме окиси двухвалентного металла или находящихся в виде кластеров в фазе, подобной Cr_2O_3 , или же распределенных в хромитной фазе, образующейся при высокой температуре. Образование этих парамагнитных частиц и их температурная устойчивость сильно зависят от природы M(II) иона и от соотношения Cr(III)/(M/II). Последовательное обнаружение с помощью ЭПР этих промежуточных частиц даёт детальную информацию о механизме разложения хроматов.