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THERMAL DECOMPOSITION AND SPECTROSCOPIC PROPERTIES OF SILVER CHROMATE

M. Cieślak-Golonka

INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY OF RARE ELEMENTS,
TECHNICAL UNIVERSITY OF WROCLAW, 50–370 WROCLAW, POLAND

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The thermal decomposition reactions of silver chromate, Ag_2CrO_4 were studied in N_2 atmosphere and air in the temperature range 293–1293 K. On the basis of the weight loss, infrared spectra, X-ray diffraction and scanning spectroscopy measurements the decomposition scheme of the compound has been proposed and the activation energy, E_a calculated. Digital filter enhanced electronic spectroscopy was used for the estimation of the band positions in the spectra of Ag_2CrO_4 and $CuCrO_4$, particularly for those corresponding to oxygen-chromium electron transfer. Attempt has been made to elucidate the correlation between thermal and spectral data.

Keywords: Ag_2CrO_4, IR spectra, reflectance spectra, scanning electronmicrographs, thermal decomposition , thermal and spectral data correlation

Introduction

In the paper by Darrie *et al.* [1] it was found that the activation energy calculated from the thermal data for magnesium and lathanide chromates can be related to the energy of their charge transfer (0 →Cr) spectra. Attempts have also been made to compare E_a values for a large group of thermally investigated Cr(III) and Cr(IV) complexes to their CT band energies [2]. In contrast to known spectral characteristics of silver chromate [3], very little has been published on its thermal decomposition [4]. As part of our interest in the physicochemical properties of Cr(VI) compounds [3, 5] we have now investigated the thermal behaviour of Ag_2CrO_4 and analysed both the intermediates and final products of its decomposition. Finally, we have evaluated also the possible correlation between the spectral and thermal properties of silver and copper chromates. The thermal data for the latter compound have been found elsewhere [6].

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Experimental

Silver chromate, Ag_2CrO_4 has been obtained methatetically in the reaction of silver nitrate with potassium chromate [7].

Copper chromate, $CuCrO_4$ has been prepared by the method described in [8].

Methods

TG and DTA studies were carried out simultaneously using a Paulik-Paulik-Erdey type derivatograph in dynamic air and nitrogen atmosphere over the temperature range 293–1273 K at heating rates of 2.5, 5 and 10 $deg \cdot min^{-1}$. It was found that only platinum crucibles were appropriate for thermal studies of silver chromate. The sample weight was 150 mg. In order to allow the further characterization of the intermediates and final pyrolysis residues, the samples were heated up to selected and well controlled temperatures, according to the information obtained earlier from the thermal curves.

The Coats-Redfern method [9] was used to evaluate non-isothermal kinetic parameters. The linear regression parameters (r) and error values (σ) were estimated with known expressions.

Diffuse reflectance spectra of Ag_2CrO_4 and its decomposition products were measured in the range 12500–47000 cm^{-1} with a Hitachi 356 UV/VIS spectrophotometer interfaced to IBM/PC/AT computer. The spectra of Ag_2CrO_4 were recorded in Li_2CO_3, KBr and KNO_3 matrices.

The variable digital filter method [10–12] has been applied for the analysis of the poorly resolved spectra of silver chromate. The filtration has been made for various combinations of energy ranges, distances between measured points (in cm^{-1}) and filter parameters α and N [10].

Additionally, to evaluate the thermal-spectroscopic relations, $CuCrO_4$ has been obtained [8] and its diffuse reflectance spectra recorded. The filtration has been made for $CuCrO_4$ spectra in Li_2CO_3. The E_a data for $CuCrO_4$ (from thermal analysis) were taken from the literature [6].

The infrared spectra were recorded by a SPECORD 80 instrument in the 400–2500 cm^{-1} spectral range using both Nujol mull and KBr pellets.

The X-ray patterns of the solid intermediates and final residues were obtained on a DRON-2 diffractometer with a CoK_α radiation lamp.

Scanning electron micrographs were made with a Stereoscan 180 Cambridge apparatus.

Results and discussion

Thermal decomposition of Ag_2CrO_4

The scanning electron micrographs of the substrate when magnified 10000 times (Fig. 1) showed Ag_2CrO_4 to form very small crystallites. The microscopic measurements of the intermediates and end products of the decomposition complement the results provided by other methods. The electronic spectra of the products were not very informative because of the reflection due to metallic silver, one of the products of decomposition. Tables 1 and 2 show the temperature ranges and percentage mass losses of the particular decomposition stages together with proposed reaction stoichiometries. Previous information on the thermal decomposition of silver chromate recorded in a limited temperature range (up to 973 K) [4] revealed that the compound exhibits a reversible polymorphic transition at 766 K and its melting temperature is 938 K. Our studies (Table 3) generally confirmed these results. Unfortunately, we have not observed the exothermic peak at 623 K which has been ascribed to an irreversible polymorphic transition.

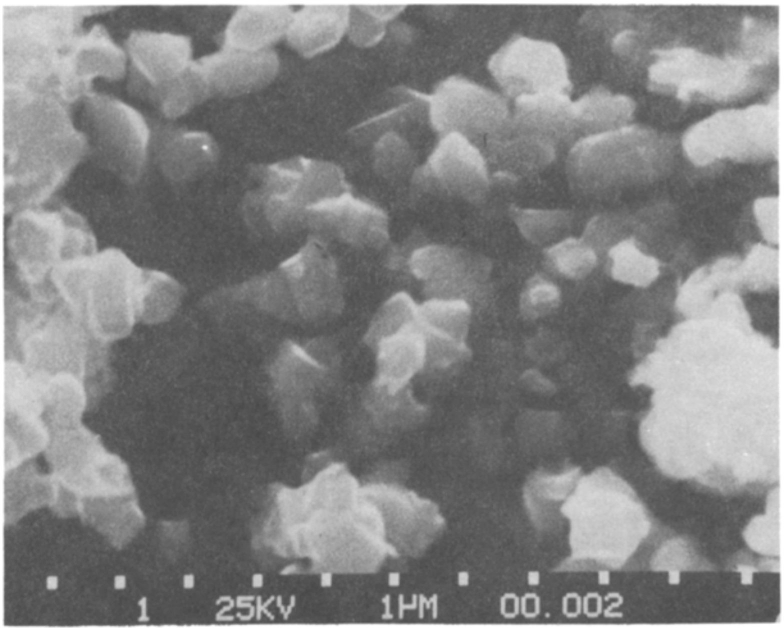

Fig. 1 Scanning electron micrograph of Ag_2CrO_4 (magnification 10000×)

The results show (Tables 1 and 2, Fig. 2) that silver chromate decomposes on heating with a gradual loss of oxygen and the oxidation number of chromium is reduced from 6 to 3. The comparison of the data obtained for air and inert atmos-

Table 1 Proposed reaction stoichiometries for Ag_2CrO_4 in N_2 at various heating rates β

Stage	β / min	TG / K	DTG peak	Weight loss / % Found	Weight loss / % Calcd.	Reaction
I.	2.5	363–973	913	10.13	9.66	$Ag_2CrO_4 \rightarrow AgCrO_2 + Ag + O_2$
			933			
	5.35	453–923		4.3	4.8	$Ag_2CrO_4 \rightarrow Ag_2CrO_3 + 0.5O_2$
		923–973		6.1	5.07	$Ag_2CrO_3 \rightarrow AgCrO_2 + Ag + 0.5O_2$
	10.0	513–923	913	1.73	1.92	$Ag_2CrO_4 \rightarrow Ag_2CrO_{3.6} + 0.2\ O_2$
		923– 1073	1073	8.68	7.86	$Ag_2CrO_{3.6} \rightarrow AgCrO_2 + Ag + 0.8O_2$
II.	2.5	1073– 1193	1183	2.2	3.3	$2AgCrO_2 \rightarrow Ag_2Cr_2O_{3.2} + 0.4O_2$
		1193– 1273	1223	0.3	0.8	$Ag_2Cr_2O_{3.2} \rightarrow Cr_2O_3 + 2Ag + 0.1O_2$
	5.35	1073– 1193	1183	2.08	3.35	$2AgCrO_2 \rightarrow Ag_2Cr_2O_{3.2} + 0.4O_2$
		1193– 1273	1243	0.6	0.8	$Ag_2Cr_2O_{3.2} \rightarrow Cr_2O_3 + 2Ag + 0.1O_2$
	10.0	1093 – 1223	1213			(TG curve weakly resolved)
		1223 – 1273	1253			

Table 2 Proposed reaction stoichometries for the thermal decomposition of Ag_2CrO_4 in air at various heating rates β

Stage	β / min	TG / K	DTG peak	Weight loss / % found	Weight loss / % calcd.	Reaction
I.	2.5	293–913	913	1.8	2.4	$Ag_2CrO_4 \rightarrow Ag_2CrO_{3.5} + 0.25O_2$
		913–1033	1023	5.5	4.95	$Ag_2CrO_{3.5} \rightarrow Ag_2CrO_{2.5} + 0.5O_2$
		1033–1063	1053	2.4	2.6	$Ag_2CrO_{2.5} \rightarrow AgCrO_2 + Ag + 0.25O_2$
	5.0	313–923	1033	4.68	4.82	$Ag_2CrO_4 \rightarrow Ag_2CrO_3 + 0.5O_2$
		923–1073	1083	4.06	5.06	$Ag_2CrO_3 \rightarrow AgCrO_2 + Ag + 0.5O_2$
	10.0	423–1033	1033	3.88	3.86	$Ag_2CrO_4 \rightarrow Ag_2CrO_{3.2} + 0.4O_2$
		1033–1133	1093	6.69	6.02	$Ag_2CrO_{3.2} \rightarrow AgCrO_2 + Ag + 0.6O_2$
II.	2.5	913–1213	1213	2.3	2.08	$2AgCrO_2 \rightarrow Ag_2Cr_2O_{3.5} + 0.25O_2$
		1213–1273	1253	1.8	2.07	$Ag_2Cr_2O_{3.5} \rightarrow Cr_2O_3 + 2Ag + 0.25O_2$
	5.0	1093–1273	1253	4.69	4.16	$2AgCrO_2 \rightarrow Cr_2O_3 + 2Ag + 0.5O_2$
	10.0	1132–1223	1233	2.09	2.08	$2Ag_2CrO_2 \rightarrow Ag_2CrO_{3.5} + 0.25O_2$
		1223–1273	1263	2.13	2.08	$Ag_2Cr_2O_{3.5} \rightarrow Cr_2O_3 + 2Ag + 0.25O_2$

phere revealed that the thermal behaviour of silver chromate is similar in both atmospheres. However, the reduction process in air is slower.

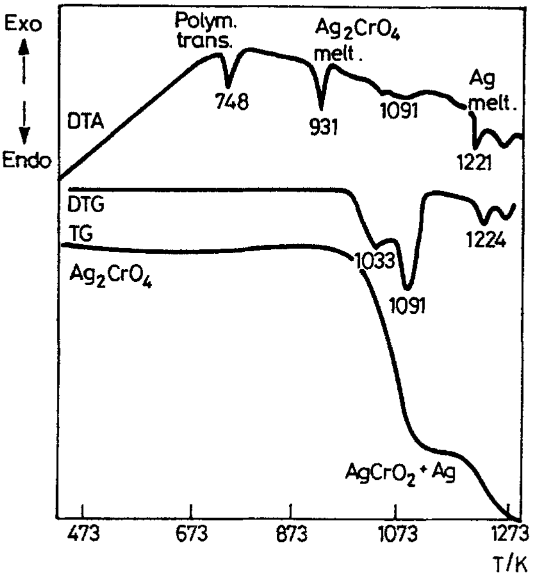

Fig. 2 TG, DTG and DTA curves of Ag_2CrO_4 in air at β = 10 deg·min^{-1}

The thermoanalytical data show that the decomposition reaction proceeds in two main stages according to the general reactions:

$$Ag_2CrO_4 \rightarrow AgCrO_2 + Ag + O_{2(g)} \qquad \text{Stage I} \quad (1)$$

$$AgCrO_2 \rightarrow 0.5Cr_2O_3 + Ag + 0.25O_{2(g)} \qquad \text{Stage II} \quad (2)$$

Often each system is divided into two or three well defined substages (Tables 1 and 2). These substages correspond to the formation of intermediate, non-stoichiometric silver chromates, with chromium oxidation number lower than 6. Non-stoichimetry of these compounds is purely formal as it is calculated from the mass loss. However, the presence of relatively stable chromates with chromium oxidation numbers of 5 and 4 is well established in the literature [13–16]. All the decomposition reactions are endothermic in both air and nitrogen atmospheres. The mixture of silver metachromite and silver as solid intermediates of the decomposition (Stage I) was found with X-ray measurements. The scanning electron micrograph taken of solid intermediates isolated at 1123 K and magnified 3000 times (Fig. 3) shows the presence of two clearly defined phases: a grey one containing chromium accompanying the shining phase of metallic silver.

Figure 4 presents the infrared spectra for the intermediates and final products of silver chromate decomposition. The envelope of (1) i.e. two prominent bands

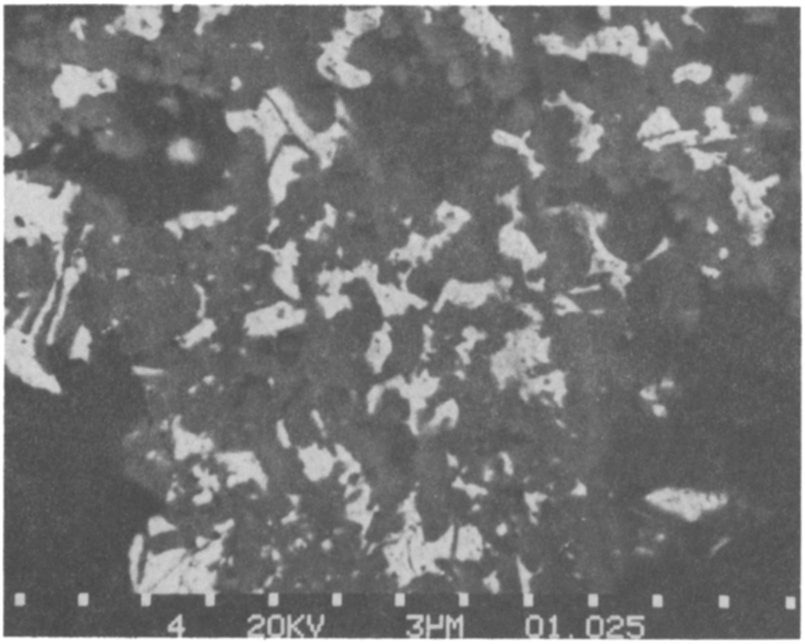

Fig. 3 Scanning electron micrograph of Stage I solid residue

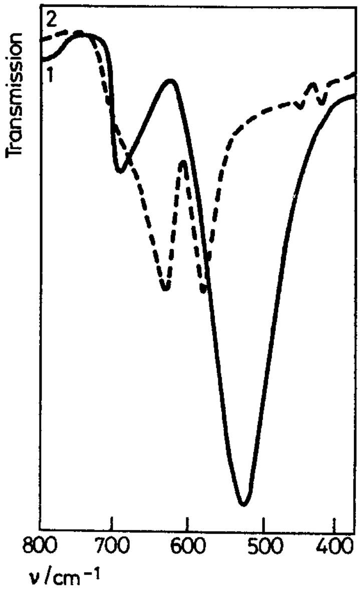

Fig. 4 IR spectra of intermediate (1 ——) and final (2 – – –) chromium containing thermal decomposition products

at 510 and 680 cm^{-1} of the intermediates are very similar to the spectrum of $HCrO_2$ [17] and thus were assigned to silver metachromite. It means that the resulting intermediate is rather $AgCrO_2$ than $Ag_2Cr_2O_4$. In the spectrum of the latter there are series of bands in the spectral region 400–700 cm^{-1} [18]. Chromites as intermediates of metal chromate decomposition have been proposed previously for $CuCrO_4$ [6] and $ZnCrO_4$ [18].

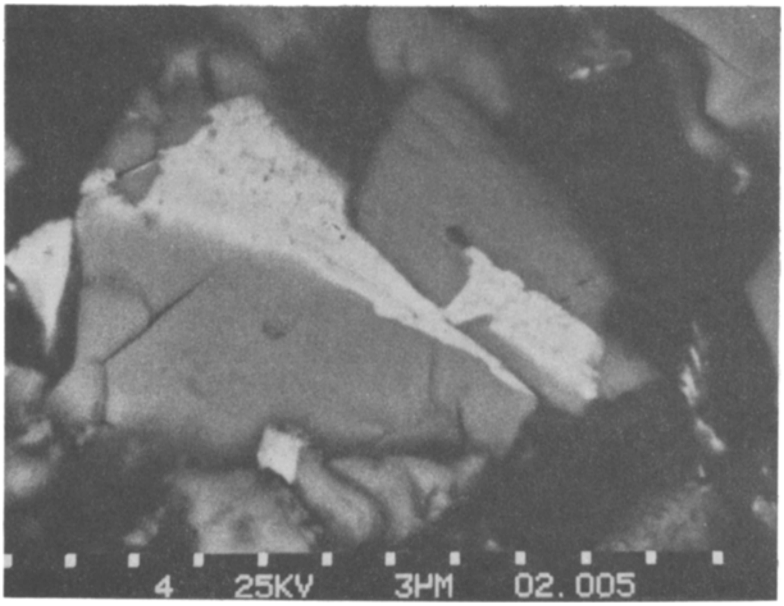

Fig. 5 Scanning electron micrograph of final residue of Ag_2CrO_4 decomposition (magnification 3000×)

Scanning microscopic (Fig. 5) and powder diffraction data showed the formation of a mixture of silver and chromic(III) oxide Cr_2O_3 as final residue of the thermal decomposition of silver chromate at 1273 K. (The scanning microscope (Fig. 5) revealed also the presence of a small amount of a third phase, most probably due to the incompletely transformed non-stoichiometric product containing chromium. The IR spectrum is shown in Fig. 4 (2). The observed band positions of (2) at 625, 570 cm^{-1} as well as the weaker ones at 411 and 440 cm^{-1} were assigned to chromium(III) oxide Cr_2O_3 [1]. The mixture of metal and chromic(III) oxide as final products of the thermal decomposition seems to be unique among the chromate salts.

Kinetic analysis of the experimental TG curves was performed and the activation energies evaluated using the well known Coats-Redfern equation [9]. The regression analysis has been performed for each tested mechanism. Generally, the selection of one kinetic model for a chosen stage and heating rate was practically impossible. This confirms the results found for the analysis of $[Co(NH_3)_6]Cl_3$ [20], namely that the studies lead to unambiguous conclusions only under isothermal conditions. Fortunately, in Stage I which is crucial for our purposes in nitrogen atmosphere a phase boundary process (R_1) with E_a = 200.0 kJ·mol^{-1} (16700 cm^{-1}) appears to be the kinetic model best fitting the experimental data. R_1 describes the decomposition process with zero-order mechanism (Polanyi-Wigner equation [19]). Unfortunately, the decomposition in air can be described alternatively with more than one model. However, if the process fulfils the requirements for summarizing the E_a values for the substages which sometimes happens [21], the E_a in air is equal to 199 kJ mol^{-1} (16620 cm^{-1}).

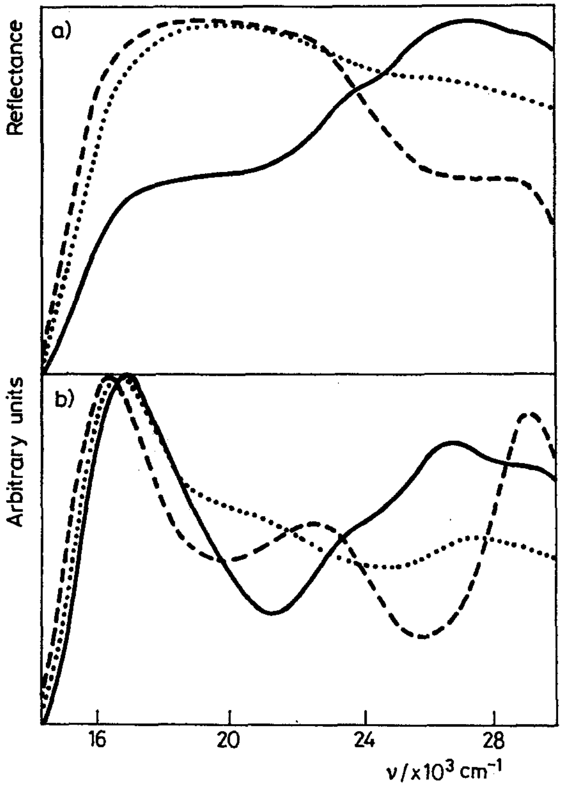

Fig. 6 Diffuse reflectnce spectra of Ag_2CrO_4 in various matrices — (a) and filtering of the curves — (b).
(a) — spectra in Li_2CO_3 (· · ·), KBr (—) and KNO_3 (– – –), (b) — filtration with the following filter parameters: $\alpha = 100$; $N = 50$

Thermal and spectral relations

In contrast to alkali metal chromates, the silver salt is dark brown. There were some attempts in the literature to explain the unusual colour of silver chromate [3]. At present it is clear that the Ag–O (CrO_4) covalent interaction is responsible for the large (10000 cm^{-1}) bathochromic shift of the longest wave CT ($2e \leftarrow 1t_1$) Cr ← 0 transition (at 27000 cm^{-1} for K_2CrO_4) [3]. Unfortunately, in Ag_2CrO_4 this effect is accompanied by a strong matrix effect [22] causing a partial replacement of labile Ag^+ ions. This makes the spectra very poorly resolved. The application of the variable digital filter method showed that despite various absorption envelopes of the spectra (Fig. 6), the position of the longest wave CT band is remarkably stable, being 17400 cm^{-1} for KBr and Li_2CO_3 matrices and 17000 for KNO_3 matrix.

Table 3 Peak temperatures / K of the DTA curves for Ag_2CrO_4, recorded at different heating rates in air and nitrogen

Peak	Air / β·min			N_2 / β·min			Phenomenon
	2.5	5	10	2.5	5	10	
A	744	745	748	743	743	745	polymorphic transition
B	925	929	931	913	928	931	Ag_2CrO_4 melt. and decomposit.
C	1048		1053		981	1053	
D	1063	1083	1091			1078	Ag_2CrO_x decomp.
E	1213	1215	1221	1178	1201		$AgCrO_2$ decomp. and Ag melting
F		1243	1263	1229	1223	1223	

On the basis of their structure the chromates have been divided into two types [18]: type *a* — where particular CrO_4 entities were separated by the cations (alkali metal chromates) and type *b* — where the rows of anions were surrounded by the rows of the strongly polarizing cations (transition metal chromates). Silver chromate belongs to those of the *b* type symmetry [18]. The rows of CrO_4 tetrahedra are linked together by parallel chains of the silver ions. This arrangement is characteristic of orthorhombic $CrVO_4$ structure. According to the suggestion of Darrie *et al.* [1] the activation process of the decomposition of the b-type chromates can be propagated along CrO_4 tetrahedra and in such particular cases may be related to a one-electron reduction of Cr(VI). The strong polarizing effect of cations favours further reductions, $Cr^{5+} \rightarrow Cr^{4+} \rightarrow Cr^{3+}$. Thus in such cases we made efforts to compare E_a calculated from thermal data with the CT energy of the longest-wave ($2e \leftarrow t_1$) transition. In the case of silver chromate where E_a values were found to be 200.0 kJ·mol^{-1} this comparison seems to be satisfactory (Table 4).

Table 4 Comparison of activation energies and electron transfer in various chromate salts

Compound	Activation energy / cm^{-1}	Energy of CT transition / cm^{-1}	Ref.
$MgCrO_4$	27600 ± 1400	27000	[1]
$La_2(CrO_4)_3$	26900 ± 2800	26700	[1]
$Nd_2(CrO_4)_3$	27600 ± 1700	26700	[1]
$Sm_2(CrO_4)_3$	23100 ± 2100	23100	[1]
$CuCrO_4$	20735^a, 19127^b	23750 (in Li_2CO_3)^d	
Ag_2CrO_4	16700^c	17000 (in KNO_3);^{d} 17400 (in Li_2CO_3 and KBr)^d	

[a, b] — data from Ref. [6] for air and nitrogen, resp.

[c] — this work, Stage I (R_1), data for nitrogen atmosph.

[d] — this work, mean values of band position for 25 filtering

Recently Hanic *et al.* [6] have obtained the activation energy values for copper chromate using an isothermal TG method. These values were found to be E_a = (248±8) kJ·mol^{-1} and E_a = (229±8) kJ·mol^{-1} in air and nitrogen, respectively. However, the authors were not able to observe any relations to spectral data since copper chromate, similarly to the silver salt, exhibited a very broad band in the visible absorption range. We have recorded the diffuse reflectance spectra of $CuCrO_4$ and have made digital filtration. In the 12200–32000 cm^{-1} spectral range where one unresolved band occurs, the filtered spectra exhibit absorption at 13000, 18700 and 23500 cm^{-1}. While the first one of the lowest energy and intensity was associated with the d-d transition in the CuO_6 octahedron, the nature of the 18700 cm^{-1} band should be interpreted with care. It could reflect a tetragonal distortion of the CuO_6 octahedron where three d-d transitions can be expected [23] instead of one or as the electric dipole forbidden $^1T_1$ state in the chromate ion, by analogy with K_2CrO_4 spectra. Although we prefer the first interpretation, the other one cannot be excluded. The most prominent transition in $CuCrO_4$ appears to be the 23700 cm^{-1} absorption band. The relation of thermal and spectral data for $CuCrO_4$ are presented in Table 4 along with Hanic data for the former. If our calculation assignment is correct, the relation of the activation and CT energies, although somewhat worse than in the case of silver chromate under assumption of the R_1 model, is close to the limit observed by Darrie for lanthanum chromate [1].

Conclusions

In contradiction to the electronic absorption studies which analyse excitation between well defined donor and acceptor levels, thermal data provide rather bulky values. In some cases, however, it may be possible to relate these data, e.g. when the activation energy is connected with a charge transfer process. Thus the two experiments may provide complementary information and sometimes can verify one another. To explore this complementarity one may, however, note that

- no 'mechanically' calculated correlation exists
- the studies should provide unambigous data which are difficult to obtain from non-isothermal experiments and poorly resolved electronic spectra
- the activation energy is related to the electron transfer processes for particularly well defined a structural arrangement of molecules
- such relationship can be expected for relative simple chemical systems.

From the studies presented in this paper it can be concluded that such relations although sometimes valid for a given class of compounds, has a rather limited range.

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Zusammenfassung — In einer Stickstoff- und in einer Luftatmosphäre wurden im Temperaturbereich 293–1293 K die thermischen Zersetzungsreaktionen von Silberchromat Ag_2CrO_4 bestimmt. Anhand der prozentuellen Gewichtsverluste, der IR-Spektren, von Röntgendiffraktions- und Scanning-Spektroskopiemessungen wurde ein Zersetzungs-schema für diese Verbindung entwickelt und die Aktivierungsenergie E_a berechnet. Mittels Elektronenspektroskopie mit Digitalfilterung wurden die Bandenpositionen in den Spektren für Ag_2CrO_4 und $CuCrO_4$ geschätzt, besonders für diejenigen Banden, die dem Sauerstoff-Chrom Elektronentransfer entsprechen. Weiterhin wurde versucht, eine Beziehung zwischen thermischen und Spektraldaten zu finden.