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THERMAL DECOMPOSITION OF SILVER CHROMATE COMPLEX WITH 1, 10 PHENANTHROLINE, $Ag_2(PHEN)_2CrO_4$

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The decomposition of silver chromate complex with 1, 10 phenanthroline has been studied by TG/DTG/DTA method and X-ray diffraction analysis. Intermediate decomposition products have been isolated and characterized. The thermolysis of $Ag_2(phen)_2CrO_4$ occurs in the two major stages: $Ag_2(phen)_x"CrO_4"$ as a product of the first stage and various mixtures of silver, silver chromate and silver metachromite as the final residue. The comparison of the decomposition process of the complex with that of parent Ag_2CrO_4 indicates that the presence of ligand changes thermal behaviour of the latter.

Syntheses and spectral properties of silver chromate complexes with heterocyclic bases (HB) have been studied recently [1].We have extended this work using thermogravimetric and DTA analyses on $Ag_2(bpy)_2CrO_4$ and $Ag_2(phen)_2CrO_4$ [2]. This paper reports details on the thermal behaviour of the phen complex together with the analysis of the intermediate products of its decomposition. As various Cr(VI) compounds were found to be precursors of widely adopted chromia catalysts [3, 4], $M(HB)_xCrO_4$ type complexes can be also interesting from this point of view.

Experimental

Silver chromate complex with phen has been isolated according to the procedure described previously [1]. $Ag_2(phen)_2CrO_4$ and final products of its decomposition in air and argon atmospheres at heating rates q = 2.5, 5 and 10 deg/min as well as the intermediate residues obtained at 220, 415, 650 and 840° were examined by X-ray diffraction (DRON-2 diffractometer). TG, DTG and DTA analyses were carried out simultaneously with derivatograph (MOM, Budapest)

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Results and discussion

Thermal decomposition in argon

Two major stages are observed during the decomposition process of the complex when heated in argon atmosphere (Table 1):
(i) temperature range from 0 to 400° (stage I)
(ii) temperature range from 400 to 1000° (stage II)

Table 1 Thermal decomposition of $Ag_2(phen)_2CrO_4$ in argon at q = 2.5 deg/min

St	Peak temp. DTA, °C	Temp. range of TG, °C	Mass loss, % obs.	calcd.	Reaction
I_a	240	20-220	6.0	5.2	$Ag_2(phen)_2CrO_4 \rightarrow Ag_2(phen)_{1.8}CrO_4 + 0.2phen$
I_b	270	220-350	32.97	32.95	$Ag_2(phen)_{1.8}CrO_4 \rightarrow Ag_2(phen)_{0.6}"CrO_4" + 1.2phen$
II		350-1000	33.67	28.22	$2Ag_2(phen)_{0.6}"CrO_4" \rightarrow AgCrO_2 + Ag_2CrO_4 + Ag + O_2 + 1.2phen$

Stage I can be significantly divided into two substages I_a and I_b with $Ag_2(phen)_{1.7}CrO_4$ as an intermediate, non-stoichiometric product of the first and $Ag_2(phen)_{0.5}"CrO_4"$- of the second substage (x are slightly dependent upon q, heating rate and the atmosphere). As the oxydation state of chromium is supposed to be lower than six, the anion has been presented in the quotation marks. Moreover, various chromium to oxygen stoichiometry can not be excluded [3, 5]. Generally, stage I can be identified as partial decomposition of the complex, volatilization and decomposition of phen and finally oxidation of its products. The analysis of the DTA curves shows that stage I composes of two exothermic reactions (well developed two peaks at $q = 2.5$ and 5 deg/min, one peak with shoulder at $q = 10$ deg/min). The main loss of ligand takes place during I_b i.e. the breakdown of coordinated phen, its melting and decomposition followed by final oxydation of the decomposition products.

Two overlapping reactions are expected at stage II. The observed loss of weight indicates that 0.5-0.6 mole of phen is not volatilized until 400° and in higher temperature converted to an involatile, polymeric product(s) which is then transferred to gaseous compounds. This process should be accompanied by the reaction of silver chromate decomposition. The X-ray analysis of the residue at 1000° shows presence of the following mixtures: $AgCrO_2 + Ag$, $Ag_2CrO_4 + Ag$ and $AgCrO_2 + Ag_2CrO_4 + Ag$ as final products

at 10, 5 and 2.5 deg/min, respectively. That means that phen under inert gas condition prevents silver chromate decomposition or gives products various than these observed during the final decomposition of Ag_2CrO_4 itself i.e. $AgCrO_2 + Ag$ [5].

Thermal decomposition in air

The X-ray analysis points that at 220° i.e. at the end of I_a, the residue contains mainly silver chromate as a crystal phase. However, the X-ray pattern for the sample obtained at 400° shows metallic silver as the crystal phase only. That means that burning of phen between 200-400° (I_b) accompanies a serious chromate ion disturbance. We propose the following formulae: $Ag_x(phen)_{0.5}$"CrO_4" for the product found at 400°. Clearly, a decay of the crystalline phase can be a process proceeding in the first stage through an intermediate, amorphous phase. The diffractograms obtained at 650° and 850° show on the presence of silver metachromite, $AgCrO_2$ with the reduced chromium ion (VI→ III), followed by formation of Cr_2O_3, which has been found as the main final product of $Ag_2(phen)_2CrO_4$ decomposition in air. It should be mentioned that small amount of metallic silver was found even at 220°.

The decomposition in air results in the weight loss of 69% whereas in argon the loss is only 58%. The difference is too large to be interpreted only by various decomposition products: in argon $AgCrO_2$, Ag_2CrO_4 Ag in air Cr_2O_3, Ag. The reason for the difference between observed and calculated final mass losses can be the explosion-type reaction characteristic of chromate and dichromate complexes [5, 6]. The various decomposition schemes in both atmospheres are seen in the DTA curves. A practically smooth DTA curve is observed in the 400-1000° temperature range in argon while two large exothermic peaks above 400° are found in air (Figs 1 and 2). It is also likely, that in air the process involves new volatile products of decomposition among which chromium and/or silver ones can not be excluded. Both in air and argon sharp, small endothermic peak at 950-970° can be assigned to the process of silver melting.

Kinetic studies

We have applied Coats-Redfern method for calculation of activation energy E_a for the first stage of complex decomposition (I). The magnitude of correction coefficient (cc) was used as a criterion for E_a chosing. The ob-

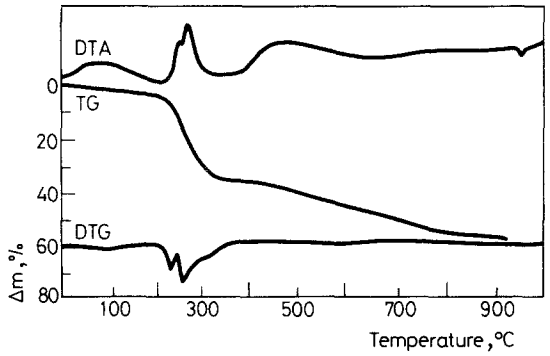

Fig. 1 Thermal curves of $Ag_2(phen)_2CrO_4$ in argon at $q=5$ deg/min and sample mass 100 mg

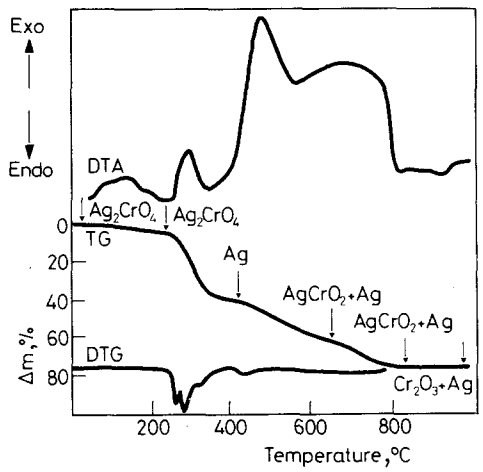

Fig. 2 TG, DTG, DTA curves of $Ag_2(phen)_2CrO_4$ in air at $q=10$ deg/min and sample mass 100 mg. Arrows point to the composition of the crystal phase

tained values for activation energy are 78.05 kJ/mol and 76.66 kJ/mol for the sample in air and argon, respectively. We have found most repeatable results for thermal curves in argon at the lowest speed of sample heating.

Conclusions

a) silver chromate complex with phen, similarly to previously studied with bpy, decomposes thermally into several stages and substages

b) chromium (III) oxide and silver were found as final products in air whereas silver chromate, silver metachromite and metallic silver- in argon

c) chemical composition of products at 1000° in argon depends upon heating rate of the sample

d) during the decomposition process we have not found for chromium other than six or three oxidation state. This problem is still under our consideration

e) the presence of ligand strongly affects on the decomposition scheme of Ag_2CrO_4

f) Coats-Redfern method applied for calculation of activation energy for stage I gave E_a 78.05 and 76.66 kJ/mol for the sample in air and argon, respectively.

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Zusammenfassung — Mittels TG/DTG/DTA und Röntgendiffraktionsanalyse wurde die Zersetzung des Silberchromat/1,10-Phenanthrolinkomplexes untersucht. Zwischenprodukte dieser Zersetzung wurden isoliert und beschrieben. Die Thermolyse von $Ag_2(phen)_2CrO_4$ verläuft in zwei Hauptschritten: im ersten Schritt entsteht $Ag_2(phen)_x$"CrO_4", als Endprodukt entstehen verschiedene Gemische aus Silber, Silberchromat und Silbermetachromit. Ein Vergleich des Zersetzungsprozesses des Komplexes mit dem der Stammverbindung Ag_2CrO_4 ergab, daß die Gegenwart von Liganden das thermische Verhalten von Ag_2CrO_4 verändert.