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THERMAL DECOMPOSITION OF SILVER CYANO COMPLEX AND CHARACTERIZATION ITS DECOMPOSITION PRODUCTS BY ETA, DSC, DTA AND TG*

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It was found by DTA and TG that [Phenyl$_2$I][Ag(CN)$_2$] in the solid state is chemically stable on heating in argon up to 160°C. During heating to higher temperatures it decomposes, forming volatile products such as [Phenyl]I, [Phenyl]NC and (CN)$_2$ [1]. After heating the sample to 500°C metallic silver resulted. The volatile and intermediate solid products were analysed by IR-spectroscopy.

It was found by means of DTA and ETA that an isophase reversible transition takes place when the sample is heated and cooled, not higher than 100°C. At heating higher than 100°C the sample melts (melting point T_m=135°C). The enthalpy melting was determined by means of DSC (ΔH=–28 kJ·mol^{-1}).

By means of ETA the disorder degree of the final decomposition product was estimated. The value of the activation energy of radon diffusion in the temperature range 720°–500°C equals 32.6 kJ·mol^{-1}.

Keywords: ETA, DSC, DTA, silver cyano complex, TG

Introduction

The silver cyano complex with phenyliodonium cation [Phenyl$_2$I][Ag(CN)$_2$] possessing a biological activity, was prepared for the first time at the Department of Inorganic Chemistry, Šafarik University, Košice.

The thermal stability of this compound as well as the thermal behaviour of the reaction products are studied in this paper. Thermogravimetry (TG) and differential thermal analysis (DTA) were used for thermal stability testing, DSC was used for the determination of enthalpy changes during heating. The ETA was used for indication of the structure disorder of intermediate and final prod-

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ucts of the thermal treatment. Infrared spectroscopy and chemical analysis were used for determination of chemical composition of the intermediate and final products.

Experimental

Preparation of samples

The samples were prepared by the reaction of saturated aqueous solution of $[Ph_2I]Cl$ and aqueous solution of the silver alkaline cyano complex in stoichiometric ratio at the temperature of 50°C. After 30 minutes of intensive stirring and stepwise cooling of the system, the crystals of

$[Phenyl_2I][Ag(CN)_2]$ were formed. After filtration and alcohol washing the solid crystals were dried in vacuum [2].

The samples for ETA measurement were additionally labelled by absorbing the nuclides of ^{228}Th, and ^{224}Ra on the sample surface from acetone solution. After drying the samples were reserved at least for four weeks before the ETA measurement. The spontaneous radioactive decay gives rise to atoms of ^{220}Rn according to the following scheme:

$$^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{220}Rn$$

Methods used for a samples characterisation

The prepared substances were identified by elementary analysis (CHN-analyser Hewlett Packard) and by chemical analysis of metals. The infrared spectra of solid substances, gaseous products and intermediates of thermal decomposition were measured by Specord Spectrofotometer Model 80, Zeiss Jena SRD (in the region of 400–200 cm^{-1}). The IR-measurements of the solids and gases were performed in KBr and CH_2Cl_2, resp.

The thermal properties of the substances were investigated in argon atmosphere by Derivatograph (MOM Budapest Hungary) by using DTA, TG/DTG. Sample amount 0.1 g, platinum crucibles and the heating rate 9 deg·min^{-1} were used. The emanation thermal analysis [3] of original substances and intermediate products of thermal decomposition was carried out using an ETA instrument (Institute of Nuclear Research, Rez, CSFR). The samples amounting 0.1 g were measured in corundum crucibles on the heating and cooling rates 5 deg·min^{-1} and 2.5 deg·min^{-1} resp. in argon atmosphere. The measured parameter of ETA – the radon release rate is given in relative units. The DSC measurements were

performed using NETZSCH DSC 200 in nitrogen at the heating rate 10 deg·min^{-1}, the samples amounting 4.6 mg.

Results and discussion

Behaviour of [Phenyl$_2$I][Ag(CN)$_2$] during heating in argon are demonstrated in Fig. 1.

As it follows from Fig. 1 two endothermic effects were observed on the DTA curve of [Phenyl$_2$I][Ag(CN)$_2$]. The endothermal effect at 100°C appeared both during. As first and second run heating to 125°C. It is evident from the IR spectra that the position, shape and intensity of the absorption band corresponding to the vibration ν_{CN} do not change for the sample before and after heating to 125°C (Fig. 2). Therefore we can suppose that neither structure nor symmetry of the molecule changed during sample heating. No effect was observed at 100°C on the DSC curve when using only 4.6 mg of the sample. We have suggested that on isophase second transition takes place in this region which is not accompanied by any change of enthalpy. Only the higher amount of the sample used for DTA measurement by Derivatograph gives the evidence of the C_p changes.

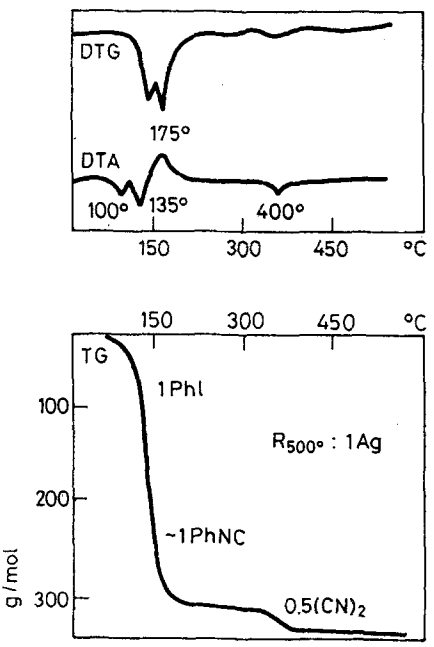

Fig. 1 TG, DTG, DTA curves of [Phenyl$_2$I][Ag(CN)$_2$]

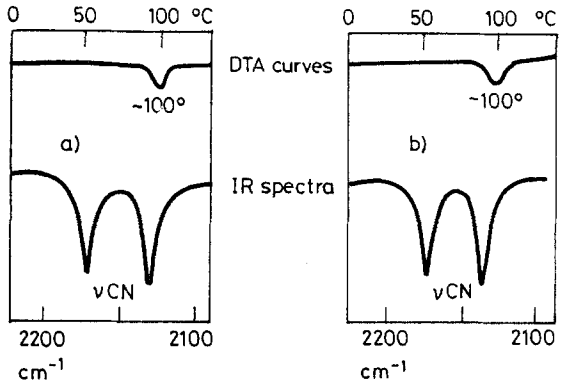

Fig. 2 IR spectra a) before heating to 125°C; b) after heating to 125°C

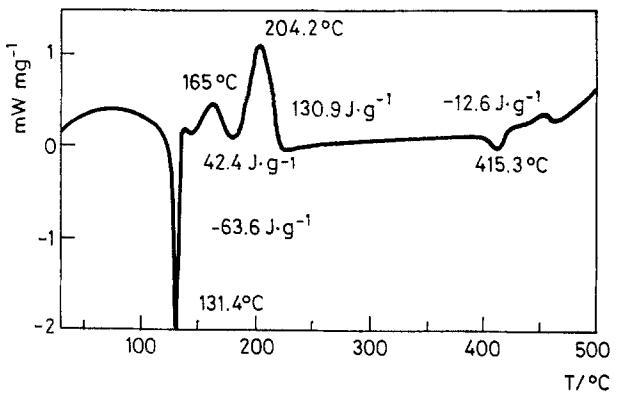

Fig. 3 DSC curve of [Phenyl$_2$I][Ag(CN)$_2$]

The second endothermal effect on the DTA curve corresponds to the melting of the original substance. The melting is represented by DSC as an endothermal effect with the minimum at 131.4°C, the enthalpy of melting was determined as ΔH=–28 kJ·mol^{-1}. The substance decomposes in the melt giving volatile products such as PhI, PhNC and (CN)$_2$. The onset on the decomposition was indicated by the DSC curve (Fig. 3) at 140°C. Maximum rate being at 165°C. The enthalpy of this changes was ΔH=18.6 kJ·mol^{-1}. The second step of the thermal decomposition, being accompanied by the release of PhNC, starts at 180°C with the maximum at 204.2°C. The enthalpy change ΔH=57.7 kJ·mol^{-1}. The two steps are not well distinguished on the TG curve (Fig. 1). On the further heating the release of (CN)$_2$ takes place at 400–420 as indicated by both DSC and DTA curves (the en-

thalpy change being ΔH=–5.5 kJ·mol^{-1}). The final decomposition product is metallic silver.

The gaseous decomposition products were distilled off and identified in CH_2Cl_2 solution by infrared spectroscopy. The solid intermediates of thermal decomposition were extracted into CH_2Cl_2 and their IR spectra were measured in the extract as well as in the residue after extraction. The IR spectra are demonstrated in Fig. 4.

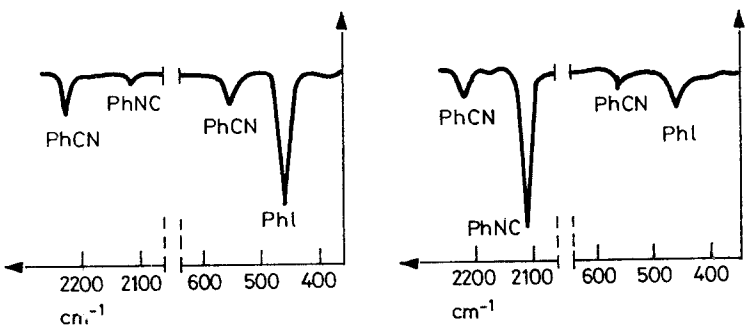

Fig. 4 IR-spectra of gaseous decomposition products in CH_2Cl_2 and solid intermediates

Characterization of the morphology changes during heating by ETA

It was of interest to complement the results of DTA and TG by the ETA results characterizing morphology changes as well as the diffusion properties of the sample during heating. The ETA curves of [Phenyl$_2$I][Ag(CN)$_2$] are demonstrated in Fig. 5.

Thermal stability range 20°–135°C.

As it follows from the temperature dependence of the radon release rate a considerable increase in diffusion mobility of radon in the solid appears at temperatures exceeding 50°C with the maximum at 98°C. It the interval of 98°–115°C the radon release rate E decreases. This change is accompanied by the reversible endothermic effect on the DTA curve Fig. 1. Therefore we may assume that morphological changes in the sample takes place within this temperature range. This structure rearrangement can be ascribed to an isophase transition. The isophase transition is indicated on the ETA curve at the 2nd heating of sample. The increase in the release rate continues on further heating in the temperature range from 115° to 135°C, giving evidence of that increased mobility in the crystal lattice. The process of melting is indicated by ETA as a de-

crease in the radon rate release which is due to the destruction of radon diffusion paths in the solid.

Thermal decomposition in the region 135°–750°C.

The DTA, TG/DTG (see Fig. 1) and infrared spectroscopy (Fig. 4) showed that thermal decomposition of the original in this region gives rise to PhI, PhNC and $(CN)_2$. The results of ETA indicated that the rate of radon release in the initial stage of decomposition in the melt increases. During heating above the temperature of 250°C the emanation release rate increases which corresponds to thermal diffusion in the intermediate product AgCN. It follows from the results obtained by TG/DTG and DTA that AgCN decomposes in the region 380°–400°C to give elementary silver which is indicated by the effect on the ETA curve.

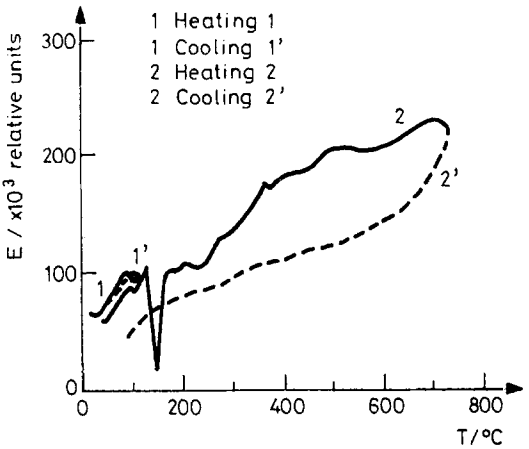

Fig. 5 ETA curves of $[Phenyl_2I][Ag(CN)_2]$

The results obtained in the region 500°–900°C by ETA reveal the changes of the morphology during sample heating above 500°C.

Characterization of $[Phenyl_2I][Ag(CN)_2]$ decomposition products by Emanation Thermal Analysis

As it follows from the ETA curve of the sample measured during non-isothermal heating (5 deg·min^{-1}) in the range from 500° to 900°C the morphology change sintering of the sample takes place. In order to characterize the thermal behaviours of the sample in this temperature interval 600°–750°C, the ETA curve were measured during isothermal heating at 640° and 760°C whereas the increase in radon release rate was observed during isothermal heating at 640°C,

indicating the loosening the lattice, the decrease of E observed during the isothermal heating at 760°C indicated the ordering of the structure due to sintering. This decrease in emanation rate measured at 760±1°C enabled us to estimate the kinetics of sintering of the decomposition product (metallic silver).

Values of activation energy Q of radon diffusion were calculated as a parameter characterizing the degree of structure disorder of material [3–5] from the ETA data measured during cooling of the samples heated to 720° and 900°C resp.

The metallic silver is in a highly disperse (active) state. The product obtained by the non-isothermal treatment in argon to 720°C is characterized by the relative low values of the activation energy of radon diffusion calculated from the slope of the curves $\log E_D = f(1/T)$, Q=32°±2 kJ·mol^{-1} calculated for the temperature interval 720°–500°C.

When the sample was heated in argon in non-isothermal condition to 900°C (melting point for silver is 960.8°C) the sintering of the metallic silver was observed on heating above 700°C with lead to the considerable decrease in the structure disorder of the sample. The activation energy of radon diffusion Q for the temperature interval 900°–750°C was found Q=144±5 kJ·mol^{-1}. This value of radon diffusion of activation energy is near to the value found for Kr and Rn diffusion in the silver compact sample obtained by Kawasaki and Matzke [6, 7].

It can be seen from the comparison of the values of radon diffusion activation energies Q for silver heated do 720° and 900°C that the heating above 720°C causes a decrease in the structure defect stage of the metallic silver prepared by the thermal decomposition of complex compound.

Conclusions

The thermal stability of [Phenyl$_2$I][Ag(CN)$_2$] and its thermal behaviour during heating in argon was studied by DTA and TG/DTG.

The compound is stable to 135°C, on further heating it melts and decomposes. It is supposed that the reversible isophase transition at the temperature of 98°C takes place in the solid complex compound accompanied by a morphology change as indicated by ETA. The enthalpies of the melting and three decomposition steps of the complex compound were determined by DSC.

The metallic silver in the active state prepared by thermal treatment of the complex compound studied was characterized by ETA from the viewpoint of the morphology changes due to sintering. The relative defect stages of the metal silver powder after heating to 720° and 900°C were estimated as the radon diffusion activation energy values (Q=32±2 and 144±5 kJ·mol^{-1}).

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Zusammenfassung — Mittels DTA und TG wurde [Phenyl$_2$I][Ag(CN)$_2$] untersucht in im festen Zustand bei Erhitzen in einer Argonatmosphäre bis 160°C als thermisch stabil befunden. Beim Erhitzen auf höhere Temperaturen erfolgt eine Zersetzungsvorgang, wobei flüchtige Produkte wie z.B. [Phenyl]I, [Phenyl]NC und (CN)$_2$ entstehen. Bei Erhitzen auf 500°C erhält man metallisches Silber. Die festen Zwischen- und flüchtigen Produkte wurden mittels IR-Spektroskopie untersucht.
Anhand der DTA- und ETA-Untersuchungen konnte festgestellt werden, daß bei Erhitzen und Abkühlen unterhalb 100°C reversible Einphasenumwandlungen stattfinden. Bei Erhitzen über 100°C schmilzt die Probe (Schmelzpunkt T_m=135°C). Die Schmelzenthalpie wurde mittels DSC ermittelt (H=–28 kJ/mol).
Mit Hilfe von ETA wurde der Unordnungsgrad des Zersetzungsendproduktes geschätzt. Der Wert der Aktivierungsenergie für die Radondiffusion im Temperaturbereich 720°–500°C beträgt 32,6 kJ/mol.