

THERMAL STABILITY OF [PHENYL₂I]⁺ CYANO COMPLEXES CONTAINING SILVER, CHROMIUM AND COBALT *

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ABSTRACT

The thermal stability of the complexes [Ph₂I][Ag(CN)₂], [Ph₂I]₃[Cr(CN)₆] and [Ph₂I]₃[Co(CN)₆] on heating in argon were studied by means of DTA and TG–DTG. The morphological changes taking place during the heating of these solid samples were indicated by means of emanation thermal analysis.

INTRODUCTION

The cyano complexes of Ag, Cr and Co with the diphenyliodonium [Phenyl₂I]⁺ cation are alleged to have biological (fungicidal) activity. The biological activity depends not only on the chemical composition of the compounds but also on their morphology in the solid state. The aim of this paper is to study the thermal stability of cyano complexes of Ag, Cr and Co with diphenyliodonium cation.

In addition to the study of the morphological changes in the solid samples during their thermal treatment, their chemical compositions were determined by means of IR spectroscopy, chemical analysis and elemental CHN analysis. The thermal behaviour of the samples was examined by TG–DTG and DTA, and the morphological changes in the solids were assessed by emanation thermal analysis.

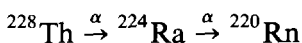
* Dedicated to Professor H.J. Seifert on the occasion of his 60th birthday.

EXPERIMENTAL

Preparation of samples

The samples for DTA, TG and DTG measurements were prepared by the reaction of a saturated aqueous solution of $\text{Ph}_2\text{I}^+\text{Cl}^-$ with a stoichiometric amount of aqueous solution of the corresponding alkaline cyano complex at 50°C . After 30 minutes of intensive stirring and stepwise cooling of the system, crystals of cyano complexes of diphenyliodonium Ph_2I^+ were formed. They were filtered, washed with alcohol and dried in vacuum [1,2].

The samples for ETA were previously labelled by adsorbing the nuclides of ^{228}Th and ^{224}Ra on the sample surface from acetone solution [3–5]. After drying, the samples were stored for at least four weeks before the ETA measurement. The spontaneous radioactive decay gives rise to atoms of ^{220}Rn according to the following scheme

*Methods used for characterizing the samples*

The prepared substances were identified by elemental analysis (CHN analyser, Hewlett–Packard) and by chemical analysis of the metals. The IR spectra of solid substances, gaseous products and intermediates of the thermal decomposition were measured using a Specord Model 80 instrument (Jena, G.D.R.) in the region of $4000\text{--}200\text{ cm}^{-1}$. The IR measurements of the solid products were performed in KBr and those of gaseous decomposition products were taken in CH_2Cl_2 .

The thermal properties of the complexes were investigated in argon atmosphere using a derivatograph (MOM, Budapest, Hungary) using DTA, TG and DTG. The samples were placed in platinum crucibles and a heating rate of 9°C min^{-1} was used. Emanation thermal analyses of the original substances and intermediates of the thermal decomposition were made using a home-built ETA instrument (Institute of Nuclear Research, Řež, ČSFR). Samples of 100 mg were measured at heating and cooling rates 5° min^{-1} and $2.5^\circ\text{C min}^{-1}$ in argon atmosphere. The measurements were performed in corundum crucibles. The measured ETA parameter, the radon release rate, is given in relative units.

RESULTS AND DISCUSSION

The thermal stability of $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ during heating in argon

The DTA and TG–DTG results for non-isothermal heating in argon are illustrated in Fig. 1. It can be seen that there are two endothermic effects on

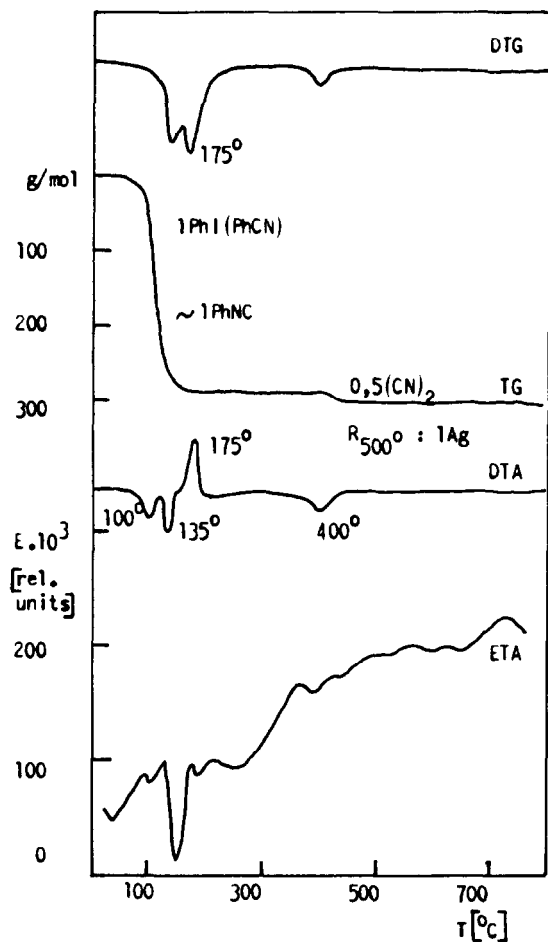


Fig. 1. The DTA, TG-DTG and ETA curves of $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$.

the DTA curve of $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ before the temperature of thermal decomposition. One peak appears at 100°C and is reversible. The IR spectra of this compound obtained before and after heating over this temperature, indicate that the position shape and intensity of the absorption band corresponding to the stretching vibration ν_{CN} do not change (2170 , 2130 cm^{-1}). This implies that neither the structure nor the symmetry of the molecule changes during the sample heating. The second endothermic peak at 135°C corresponds to melting of the original compound. The sample decomposes in the melt and the gaseous decomposition products, PhI and PhCN/PhNC, are evolved. This decomposition is indicated on the DTG curve by the double peak which can be quantitatively assigned to the liberation of one mole PhI and one mole of PhNC. The residual 0.5 mole of dicyanogen $(\text{CN})_2$ is evolved at 400°C with metallic silver as the decomposition product.

The morphological changes of $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ during heating in argon

The ETA curve of this compound is shown in Fig. 1. The thermal stability range is 20–135 °C. From the temperature dependence of the release rate of radon, a considerable increase in diffusion mobility of radon in the solid is indicated at temperatures exceeding 50 °C. In the 100–115 °C interval the rate of radon release decreases, indicating a morphological change which is also indicated by the endothermic effect on the DTA curve (see Fig. 1). This implies that morphological changes in the sample structure take place within this temperature range. This structural rearrangement can be ascribed to an isophase transition which is also indicated on the ETA curve for the second heating of the sample. The increase in the release rate continues on further heating from 115 to 135 °C, which suggests an increase in the mobility of the crystal lattice components.

The process of melting is indicated by ETA as a decrease in the radon release rate which is due to the destruction of radon diffusion paths in the solid.

DTA and TG–DTG and IR spectroscopy of the 135–750 °C region show that thermal decomposition of the original compounds in this region gives rise to PhI/PhCN , PhNC and $(\text{CN})_2$. The results of ETA indicate that the rate of radon release in the initial stage of decomposition in the melt increases. During heating from 250 °C the emanation rate increases, corresponding to thermal diffusion in the intermediate product, AgCN . From the results of TG–DTG and DTA, it can be seen that AgCN decomposes in the 380–400 °C region to give elementary silver, as is indicated on the ETA curve (Fig. 1).

The thermal stability of $[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_5\text{NO}]$ during heating in argon

Two irreversible exothermic effects, at 65 and 110 °C, appear on the DTA curve of $[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_5\text{NO}]$ (Fig. 2) before thermal decomposition. Comparing the IR spectrum of the original substance obtained at 20 °C with that of the substance heated to 80 °C (above the first exothermic effect), no change in intensity or position of the absorption bands corresponding to the stretching vibrations ν_{CN} and ν_{NO} was observed. However, if the substance is heated above the second exothermic effect (125 °C), the original split absorption band corresponding to the stretching vibrations ν_{CN} and ν_{NO} (2120, 2100, 2090 cm^{-1} ; 1675, 1630 cm^{-1}) changes into a singlet (2100; 1640 cm^{-1}). This may result from the fact that the system is stabilized because of energy release (exothermic reaction at 110 °C) and that the symmetry of the molecule has increased. The thermal decomposition starts with elimination of PhI and PhCN (190 °C, exothermic process). At higher temperatures the NO ligand is eliminated from the complex compounds. However, in contrast to some compounds containing the coordinated NO group which were studied earlier [6], this NO ligand does not enter into a secondary reaction.

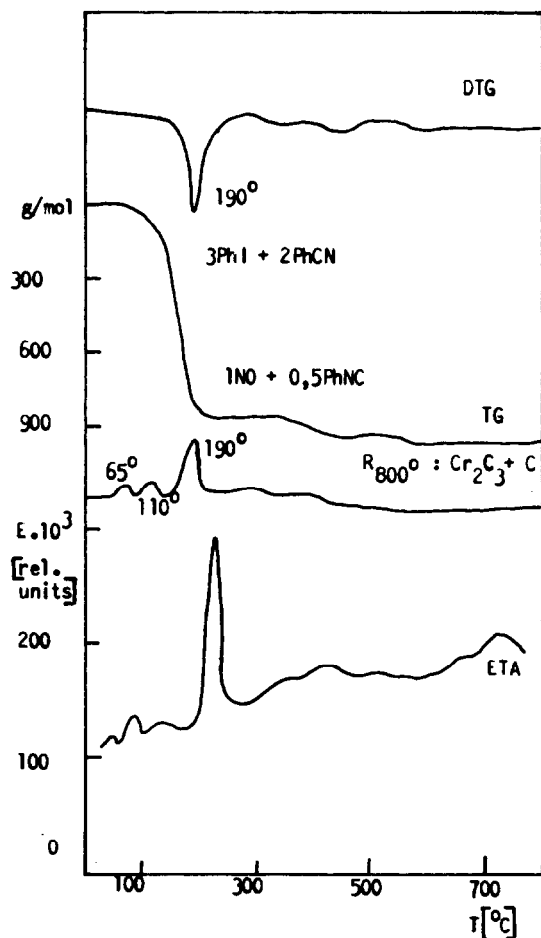


Fig. 2. The DTA, TG-DTG and ETA curves of $[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_5\text{NO}]$.

The gaseous and solid intermediates of thermal decomposition were determined by IR spectroscopy. The final product of the thermal decomposition is Cr_3C_2 and carbon.

The morphological changes of $[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_5\text{NO}]$ during heating in argon

The ETA results of this compound are illustrated in Fig. 2. Thermal decomposition does not take place in the temperature range 20–180 °C (thermal stability range). The original compound decomposes in the temperature interval 180–400 °C. Above 400 °C, only the final product remains.

Heating over 50 °C increases the radon release rate. The subsequent decreases in the radon release at 65 and 95 °C are accompanied by an exothermic effect (see DTA curve). These processes are irreversible and are thus not reflected on the ETA curve during the second heating run. Further

heating in this region brings about a significant increase in radon release rate followed by the abrupt decrease at 220 °C on the ETA curve. This effect corresponds to the evolution of 3 moles of PhI and 2 moles of PhCN, in accordance with the TG curve (Fig. 2). The TG curve shows that the subsequent heating to 400 °C leads to the liberation of NO and PhNC. These chemical processes are not obvious on the ETA curve. Therefore it can be assumed that the liberation of gaseous products of thermal decomposition is not accompanied by a change in morphology.

The ETA results indicate a morphological rearrangement of the final product (Cr_3C_2) on heating over 400 °C. Heating over 700 °C is accompanied by the sintering of the sample. This is indicated by a decrease on the ETA curve.

The thermal stability of $[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$ during heating in argon

A small exothermic effect appears on the DTA curve of $[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$ at 170 °C (Fig. 3). This effect is irreversible and is not accompanied by any change in mass (see TG curve). The IR spectrum of the original compound measured at 20 °C shows that the absorption band corresponding to the stretching vibration ν_{Cn} is markedly split (2105, 2120, 2130, 2140 and 2050 cm^{-1}). On heating to 175 °C the absorption band changes to a doublet (2100, 2110 cm^{-1}). This indicates that the symmetry of the molecule has been improved by rearrangement of the individual constituent groups. The original compound decays at 215 °C. This thermal decomposition in which 3 moles of PhI and 1 mole of PhCN are liberated, is indicated on the DTA curve as the exothermic reaction. At higher temperatures PhNC and $(\text{CN})_2$ are evolved. Metallic cobalt and carbon are the final products of thermal decomposition. The determination of the gaseous products of thermal decomposition and the solid intermediates were carried out as described above.

The morphological changes of $[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$ during heating in argon

The ETA results obtained by gradual heating of this compound in argon are shown in Fig. 3. No chemical changes take place in the sample at temperatures from 20 to 200 °C, the thermal stability range. Thermal decomposition proceeds in the temperature interval 200–500 °C. In the 500–800 °C interval only the final product of thermal decomposition is present.

In the thermal stability range, a significant increase in the radon release starts at 50 °C. The radon release rate reaches its maximum value at 100 °C and then decreases up to 170 °C. This effect does not appear on the ETA curve for the second heating run of the sample. The DTA curve shows an irreversible exothermic effect at about 170 °C which has yet to be explained: the ETA curve also shows that this effect is irreversible.

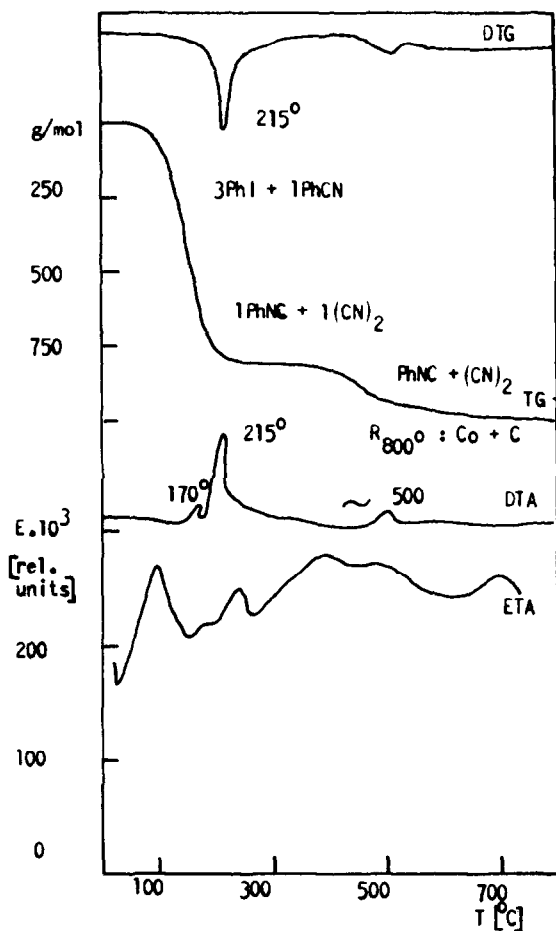


Fig. 3. The DTA, TG-DTG and ETA curves of $[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$.

On further heating, the maximum radon release rate on the ETA curve appears at 240°C . The thermal decomposition of the complex compound takes place in this region. TG measurements and IR spectra have revealed that PhI and PhCN are liberated in the first step and that PhNC and $(\text{CN})_2$ are liberated up to 500°C . Following thermal decomposition of the original compound, metallic cobalt and carbon are formed. Above 500°C , a morphological rearrangement of the high disperse material takes place. Both processes are indicated on the ETA curve by a decrease in the radon release.

CONCLUSION

$[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ is stable on heating in argon up to 135°C ; with further heating it melts and decomposes. The reversible isophase transition at

100°C takes place in the solid and is accompanied by morphological changes, as indicated by ETA.

$[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_5\text{NO}]$ is stable up to 180°C; with further heating it decomposes. During heat treatment in argon this compound undergoes two irreversible processes accompanied by exothermic effects at 65 and 110°C, as shown by DTA, and by the morphological changes indicated by ETA over these temperature intervals.

$[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$ is stable on heating up to 200°C; with further heating it decomposes. One irreversible exothermic effect was observed on heating to 170°C; this process is accompanied by morphological changes in the solids, as indicated by ETA. The morphological changes may cause the changes in the biological activity of the complex compound.

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