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THE THERMAL BEHAVIOUR OF DIPHENYLIODONIUM CYANOMETALLATES

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ABSTRACT

The thermal decomposition of the complexes $(Ph_2I)_2[Ni(CN)_4]$, $(Ph_2I)_3[Fe(CN)_6]$, and $(Ph_2I)_4[Mo(CN)_8]$ ($Ph = C_6H_5$), is studied by derivatography, thermomagnetic analysis, IR spectroscopy, and evolved gas analysis by the GC–MS technique and mass spectrometric analysis. The different steps of thermal dissociation of these complexes are discussed. Phenylisocyanide can be shown as an interesting pyrolysis product. It is not possible to obtain the intermediate cyanide/isocyanide mixed ligand complexes formed under solid state pyrolysis conditions.

INTRODUCTION

In connection with our investigations on photocatalytic systems[1, 2] we were interested in the thermo- and photochemical behaviour of cyanometallates, especially from Mo(IV) and W(IV)[3–5].

From quantumchemical calculations[6] on octacyanometallates(IV) as well as their corresponding complexes $[M(CN)_n(CNR)_n]$ ($M = Mo, W$; R = alkyl or aryl groups) a bathochromic shift of the photoreactive state of these complexes by stepwise substitution of cyano groups by arylisocyanide ligands follows. However, tetrakis-(arylisocyanide)tetracyanometallates(IV) have not been available until now. Therefore we tried to prepare this class of mixed ligand complexes by careful thermolysis and photolysis from diphenyliodonium cyanometallates

$$(Ph_2I)_n[M(CN)_{2n}] \xrightarrow[h\nu]{kT \text{ or}} [M(CN)_n(CNPh)_n] + n\,PhI$$

Firstly we investigated the thermal behaviour of different diphenyliodonium cyanometallates and the present paper deals with the thermal decomposition reactions of $(Ph_2I)_2[Ni(CN)_4]$, $(Ph_2I)_3[Fe(CN)_6]$, and $(Ph_2I)_4[Mo(CN)_8]$.

Since the extensive investigations by Willgerodt[7] and Beringer and co-workers

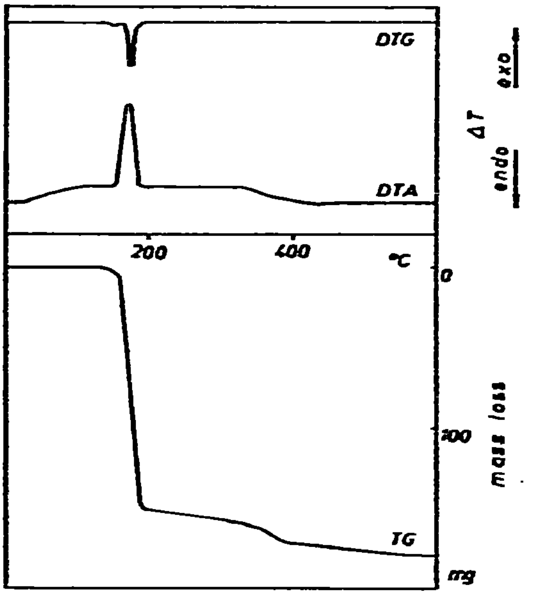
[8–12] little attention has been paid to the synthesis and properties of diaryliodonium compounds. Krause, Egen and co-workers[13, 14] reported the favourable properties of diphenyliodonium salts as precipitation reagents. They also discussed possible arylation reactions of different coordinated anions in solution as well as in the solid phase, in which they postulated reactions of intermediately formed phenyl cations with the lone pairs of coordinated ligands. These results initiated our investigations, because mixed ligand complexes with cyanide and arylisocyanide as ligands are not available by other methods, for instance by that of Novotny et al.[15].

EXPERIMENTAL

Compounds

$(Ph_2I)_3[Fe(CN)_6]$ and $(Ph_2I)_4[Mo(CN)_8]$ were synthesized by a modified procedure used by Egen and Krause[14] for $(Ph_2I)_2[Ni(CN)_4]$. To a saturated aqueous solution of diphenyliodonium chloride[17] an equivalent quantity of the appropriate potassium cyanometallate was added at 45°C. The resulting solution was cooled and left to stand in a refrigerator for some hours. The precipitated crystals were filtered, washed with a small portion of water and dried in vacuo over calcium chloride. All operations were carried out in the dark owing to the photosensitivity of the molybdenum(IV) and iron(III) complexes. Yield, about 90%; crystals, fairly good solubility in methanol, nearly insoluble in water.

$(Ph_2I)_2[Ni(CN)_4]$. Yellowish, m.p. 205°C (dec.). $C_{calc.}$ 46.4%, $C_{obs.}$ 46.7%. $H_{calc.}$ 2.79%, $H_{obs.}$ 2.86%. $N_{calc.}$ 7.73%, $N_{obs.}$ 8.20%.



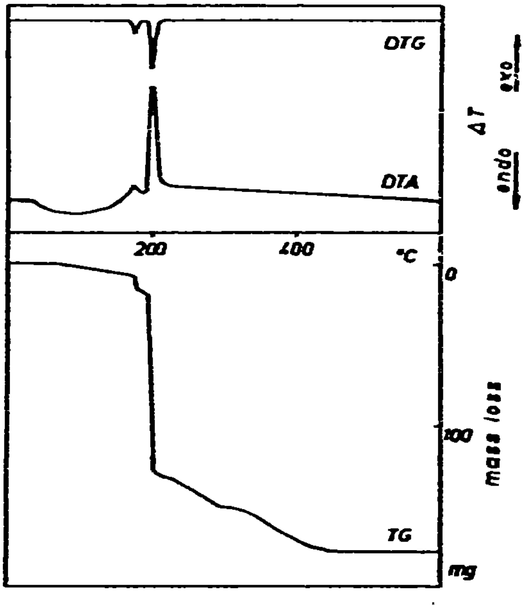
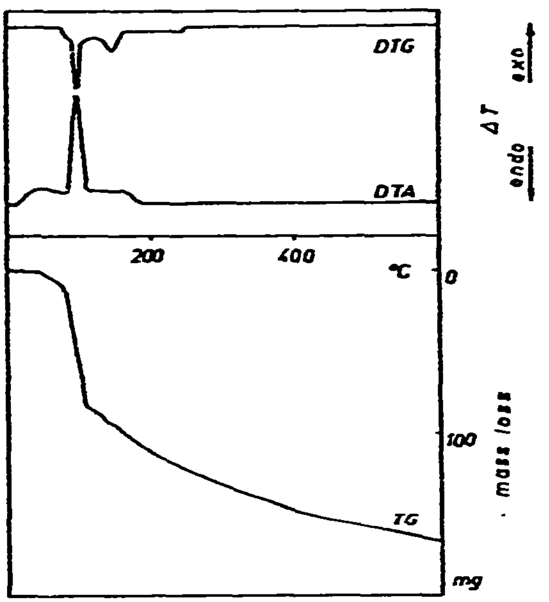


Fig. 1. Differential thermal analysis and thermogravimetric curves of $(Ph_2I)_2[Ni(CN)_4]$.

Fig. 2. Differential thermal analysis and thermogravimetric curves of $(Ph_2I)_3[Fe(CN)_6]$.



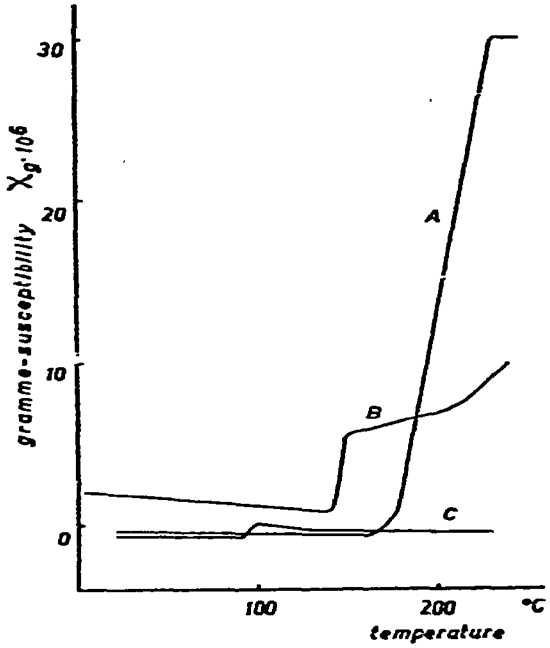


Fig. 3. Differential thermal analysis and thermogravimetric curves of $(Ph_2I)_4[Mo(CN)_8]$.

Fig. 4. Temperature dependence of χ_g for: A, $(Ph_2I)_2[Ni(CN)_4]$; B, $(Ph_2I)_3[Fe(CN)_6]$; C, $(Ph_2I)_4[Mo(CN)_8]$.

$(Ph_2I)_3[Fe(CN)_6]$. Yellow, m.p. 120°C (dec.). $C_{calc.}$ 47.8%, $C_{obs.}$ 46.15%. $H_{calc.}$ 2.86%, $H_{obs.}$ 2.64%. $N_{calc.}$ 7.87%, $N_{obs.}$ 7.97%.

$(Ph_2I)_4[Mo(CN)_8]$. Orange yellow, m.p. 80–82°C (dec.). $C_{calc.}$ 47.0%, $C_{obs.}$ 46.9%. $H_{calc.}$ 2.82%, $H_{obs.}$ 2.73%. $N_{calc.}$ 7.85%, $N_{obs.}$ 8.44%.

Thermal analysis

Thermal investigations were performed with a KOM G-425 type derivatograph. The TG, DTG, and DTA curves were registered simultaneously (Figs. 1–3). For the $(Ph_2I)_2[Ni(CN)_4]$ and $(Ph_2I)_3[Fe(CN)_6]$ complexes a very vigorous exothermic decomposition was observed and therefore a dilution with Al_2O_3 (50% of weight) was required. The following parameters were used: TG-sensitivity, 200 mg; DTG-sensitivity, 1/15; DTA-sensitivity, 1/10; heating rates, 5° min^{-1}; maximum temperature, 900°C; Pt crucible and argon atmosphere. The products of thermal decomposition were analyzed from the obtained mass losses as well as by the GC–MS technique.

Thermomagnetic investigations

Simultaneous magnetic-mass change curves were obtained from the complexes by the Gouy method with a special high temperature magnetic balance[18]. By reason of the vigorous decomposition of $(Ph_2I)_2[Ni(CN)_4]$ and $(Ph_2I)_3[Fe(CN)_6]$ these complexes could be heated only to about 250°C. All measurements were carried out at the temperatures listed (Fig. 4).

Analysis of the products of thermal decomposition

The volatile decomposition products were collected in a cooling trap at −90 °C and dried over Na_2SO_4. Since separation of the condensed thermolysis products by distillation failed, we investigated them by the GC–MS technique. A gas chromatograph of the type Chromatron 18-3 with a column PEG 20 000 (carrier gas He, temperature programme between 140 and 200 °C) and a Varian CH-6 mass spectrometer were used. Also, the complexes were decomposed directly in the mass spectrometer at different temperatures of the direct inlet system and the volatile decomposition products identified by their characteristic fragments.

IR spectra

The IR spectra of the complexes and of the nonvolatile decomposition products (in KBr) were recorded with an IR 20 spectrometer from VEB Carl Zeiss, Jena.

RESULTS AND DISCUSSION

$(Ph_2I)_2[Ni(CN)_4]$

The thermolysis of $(Ph_2I)_2[Ni(CN)_4]$ results in a mass loss at a steady rate until about 600 mg $mmol^{-1}$ complex where a change in the decomposition rate produces a change in the slope of the derivatograms (see Fig. 1). The major part of this mass loss was determined to be due to the loss of nearly 2 equivalents of $(Ph_2I)CN$, which converts immediately to diphenyl, iodobenzene, phenylcyanide, and phenylisocyanide, respectively. These results agree with previous investigations[19]

$$(Ph_2I)_2[Ni(CN)_4] \xrightarrow[\text{exothermic}]{200\text{–}350\,^{\circ}C} 2\,(Ph_2I)CN \rightarrow 2\,PhI + 2\,PhNC + Ni(CN)_2 \rightarrow Ni + (CN)_2$$

Among the thermolysis products iodobenzene and phenylisocyanide (or phenylcyanide) have been detected unambiguously by mass spectroscopy. Because the fragmentation pathways of phenylisocyanide and phenylcyanide are difficult to differentiate, we have confirmed the presence of the first compound by well defined chemical reactions. The magnetic states of the nickel ion in $(Ph_2I)_2[Ni(CN)_4]$ were monitored to temperatures up to about 250 °C (Fig. 4). Above this temperature the product started to become ferromagnetic and the reproducibility was increasingly inadequate. The complex, which was originally diamagnetic, changes its magnetic behaviour between 87 and 232 °C due to a change of symmetry from planar to octahedral or tetrahedral ($\mu_{eff.} = 3.1$ B.M. at 323 °C).

$(Ph_2I)_3[Fe(CN)_6]$

The thermal behaviour of $(Ph_2I)_2[Ni(CN)_4]$ and $(Ph_2I)_4[Mo(CN)_8]$ (see later) is characterized initially by a considerable loss of mass (see Figs. 1 and 3) connected with a violent exothermic reaction. By contrast the course of the thermal decomposition of $(Ph_2I)_3[Fe(CN)_6]$ is initially retarded. A preceeding slightly

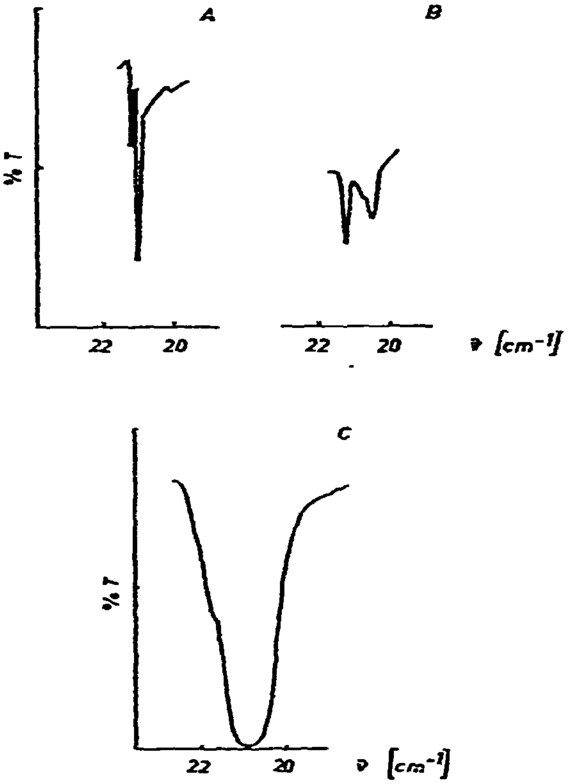


Fig. 5. IR spectra of $(Ph_2I)_3[Fe(CN)_6]$. A, before heating; B, after heating to 180 °C; C, after heating to 200 °C.

endothermic peak corresponds to the loss of 2.5 moles of water followed by a smaller exothermic step at 190 °C and by a very strong exothermic peak at 200 °C (Fig. 2).

The thermomagnetic behaviour of $(Ph_2I)_3[Fe(CN)_6]$ also points to the complicated thermal reaction of this complex in relation to $(Ph_2I)_2[Ni(CN)_4]$ and $(Ph_2I)_4[Mo(CN)_8]$, respectively[20, 21] (Fig. 4) and needs further comparative investigations of hexacyanoferrates(III) with different cations in the second coordination sphere. Obviously the discontinuity of the magnetic behaviour above 80 °C is due to an intramolecular electron transfer accompanied by the formation of cyanogen. This also follows from the sharp exothermic peak at 190 °C in the DTA and DTG curves[22].

Comparison of the IR spectra of $(Ph_2I)_3[Fe(CN)_6]$ with the corresponding thermal dissociation products also shows favouring of an intramolecular redox transition (Fig. 5). The splitting of the CN^- bands remains unchanged until temperatures of almost 180 °C. Above this temperature a single broad band at 2180 cm^{-1} can be observed, which is typical for bridging cyanide ligands. With further increase in temperature this band appears at lower frequencies and its intensity decreases, as expected for hexacyanoferrates(II)[23].

Because of the decomposition products only iodobenzene and phenylisocyanide could be detected by mass spectroscopy, the following overall reaction seems to be probable

$$(Ph_2I)_3[Fe(CN)_6] \xrightarrow[\text{exothermic}]{109\text{–}220\,^{\circ}C} 1/3[Fe^{II}_2Fe^{II}(CN)_6] + 1/2\,(CN)_2 + PhI + PhNC$$

$(Ph_2I)_4[Mo(CN)_8]$

The $(Ph_2I)_4[Mo(CN)_8]$ complex was found to dissociate at essentially lower temperatures than the compounds $(Ph_2I)_2[Ni(CN)_4]$ and $(Ph_2I)_3[Fe(CN)_6]$ (Fig. 3). The first exothermic peak at 100°C corresponds with a mass loss of 620 mg $mmol^{-1}$ complex, which could be due to the formation of 2 equivalents of iodocyane, which however we were unable to detect. Besides this reaction the formation of 2 equivalents of diphenyliodonium cyanide is also possible according to the following pathway

$$(Ph_2I)_4[Mo(CN)_8] \rightarrow (Ph_2I)_2[Mo(CN)_6] + 2\,(Ph_2I)CN$$

The formation of iodobenzene and phenylisocyanide, indicated by the mass spectroscopic investigation of the thermolysis products, speaks in favour of them. In the further course of thermal reaction 2 equivalents of phenylisocyanide (or phenylcyanide) and at last 1 mole of diphenyl are released, which could be determined unambiguously by mass spectroscopy.

Thermomagnetic analysis showed no significant change in magnetic behaviour to temperature up to 200°C. However, by ESR investigations we could obtain definite indications of molybdenum(V) formation on heated samples of the complex, obviously in very small concentration. These results will be published in connection with photochemical investigations of $(Ph_2I)_2[Ni(CN)_4]$, $(Ph_2I)_3[Fe(CN)_6]$, and $(Ph_2I)_4[Mo(CN)_8]$ complexes[16].

CONCLUSIONS

As expected, the thermal stability of the complexes described in this paper, increases in the order $(Ph_2I)_4[Mo(CN)_8] < (Ph_2I)_3[Fe(CN)_6] < (Ph_2I)_2[Ni(CN)_4]$.

The complexes described seem to dissociate in a similar manner. The first violent exothermic reaction steps are to be attributed to the intermediate formation of iodocyane, which however could not be isolated, accompanied by formation of diphenyl. The stage of ICN formation may also be connected with the formation of $(Ph_2I)CN$[19], from which in a secondary reaction iodobenzene and phenylisocyanide are formed. Lastly the corresponding metal cyanides are formed, which are usually converted into metal(0) stages, carbon and nitrogen at higher temperatures. Such reactions are not investigated here[24].

The thermomagnetic analyses confirm thermal redox processes only for $(Ph_2I)_2[Ni(CN)_4]$ and $(Ph_2I)_3[Fe(CN)_6]$ whereas the $(Ph_2I)_4[Mo(CN)_8]$ complex remains unchanged in the temperature range investigated. A thermal induced symmetry change for $(Ph_2I)_2[Ni(CN)_4]$ could be observed.

Because of experimental limitations of the Gouy method the thermomagnetic measurements could not be extended to higher temperatures.

The formation of phenylisocyanide during the thermal decomposition of $(Ph_2I)_2[Ni(CN)_4]$, $(Ph_2I)_3[Fe(CN)_6]$, and $(Ph_2I)_4[Mo(CN)_8]$ follows from the mass spectra of the decomposition products. Also the formation of phenylisocyanide could be confirmed by specific chemical reactions and its characteristic smell. Therefore it is very probable that in the course of the pyrolysis of diphenyliodonium cyanometallates a thermally formed phenyl species (cation or radical) attacks the coordinated cyanide at the nitrogen atom. Obviously the formed phenylisocyanide complexes are not conceivable under the conditions of their formation, and decompose in the described manner. On the basis of these results we will try to isolate such intermediately formed phenylisocyanide/cyanide mixed ligand complexes by controlled pyrolysis experiments in noncoordinating and inert solvents.

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