Investigation of thermal behaviour of solid transition metals cyano complexes with organic cations

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Abstract

The results obtained by the methods of thermal analysis and infra-red and Mössbauer spectroscopies are surveyed with the aim of showing the trends in the change of the thermal properties of solid cyano complexes of first and second group transition elements with the organic cations $[R_4N]^+$, $[R_3S]^+$, $[R_3Te]^+$ and $[Ph_2I]^+$.

INTRODUCTION

Various techniques of thermal analysis, mainly thermogravimetry (TG), differential thermal analysis (DTA), evolved gas analysis (EGA), including the less common techniques of thermoconductivity analysis and emanation thermal analysis (ETA) and others are often used in the investigation of complex compounds.

In recent years we have investigated the properties of complex compounds and have synthesized new cyano complex compounds of transition elements (mainly copper, silver, gold, nickel, palladium, platinum, zinc, cadmium, mercury, iron, chromium, manganese, molybdenum and tungsten), containing both the CN ligand and another one (e.g. NO, PPh_3, NH_3, dipy and phen), with the following onium cations: $[R_4N]$, $[Me_3S]$, $[Me_2PhS]^+$, $[Ph_3S]^+$, $[Ph_3Te]^+$ and $[Ph_2I]^+$.

The systematic investigation of a large number of these compounds has enabled us to find the trends in the changes of the thermal stability of the individual complex compounds with regard to the changes in the cations or in the central metal atom. Moreover, the ETA results obtained have allowed us to obtain new information on the changes that occur in the morphology of selected complex compounds during heating; this information cannot be obtained by traditional techniques of thermal analysis. In addition, using the

ETA technique we have obtained information on the kinetics of isophase transformations, the kinetics of thermal decomposition and the properties of the decomposition products of the metal complex compounds (representing the pure metal in a highly dispersed state) [1–4]. We are indebted to Professor V. Balek of the Nuclear Research Institute at Řež, who developed this technique and applied it to the investigation of various processes. It is a pleasure for us to dedicate this paper to him on his 50th birthday.

THE HISTORY OF THE INVESTIGATION OF THE CYANO COMPLEXES OF TRANSITION METALS

Thermal properties of complex compounds have been investigated by many authors. Wendlandt and Smith [5] have shown the advantages and possibilities of applying thermal analysis to the investigation of complex compounds with ammine ligands. In these studies the methods of TG/DTG, DTA as well as non-traditional techniques (EGA, mass spectrometry, thermomagnetic measurements, thermodilatometry, etc.) were used.

Our special field of interest is the investigation of cyano complex compounds. The cyano complexes of transition elements have been known for a long time, e.g. potassium ferrocyanide ($K_4[Fe(CN)_6] \cdot 3H_2O$) has been known for more than 200 years. Potassium ferrocyanide and potassium ferricyanide ($K_3[Fe(CN)_6]$) were originally prepared from slaughterhouse wastes (blood ash), iron chips and K_2CO_3. The first thermal and stoichiometric data on these compounds were presented in 1922. Perret and Gislon (1933) studied the properties of some cyano complexes and mentioned the fact that the products of their thermal decomposition depended on the type of cation involved.

More recently, the thermal properties of cyano complexes have been investigated by Mohai and Bagyin [6]. Besides the thermal decomposition of ferro- and ferri-cyanides with cations of alkali and alkaline earth metals, these workers also investigated complexes containing other central atoms. They found that not only the final products but also the initial temperature and the mechanism of thermal decomposition differed according to the type of cation. When investigating the thermal decomposition of ammonium and quaternary ammonium cyano complexes, they found that the decomposition is an exothermic process, where the acidic and alkaline components are in the ratio 1 : 1 and, in all cases (including compounds with the $[Me_3PhN]^+$ cation), alkyl cyanide is formed; besides CH_3CN N, N'-dimethyl aniline is also formed. Songstadt et al. [7] prepared methyl isocyanide by thermal decomposition of $[Ph_3MeP][Ag(CN)_2]$. Mohai and Bagyin [6] also showed that in the thermal decomposition of tetrabutylammonium dicyanoaurite and argentite butyl isocyanide is also formed. However, they did not give any interpretation of the reason for the formation of isocyanide.

TABLE 1

Secondary, tertiary and quaternary onium ions in cyano complexes

Onium cation	Cyano complex anion	Ref
$[R_2Cl]^+, [R_2Br]^+, [R_2I]^+$	$[Ph_2I]^+$	9, 7
$[R_3O]^+, [R_3S]^+$ $[R_3Se]^+, [R_3Te]^+$	$[Me_3S]^+, [Ph_3S]^+, [Me_2PhS]^+$ $[Ph_3Te]^+$	15
$[R_4N]^+$	$[Me_4N]^+, [Et_4N]^+, [Bu_4N]^+,$ $[Me_3PhN]^+$	6
$[R_4P]^+$	$[Ph_4P]^+, [Ph_3BenzP]^+,$ $[Bu_4P]^+, [Bu_3BenzP]^+,$ $[Ph_3MeP]^+$	20
$[R_4As]^+, [R_4Sb]^+$	–	

Similarly, no explanation of the formation of cyanide and isocyanide has been given by Hantchmann et al. [8] in their papers on the thermal decomposition of Fe(III), Ni(II) and Mo(IV) diphenyliodonium cyano complexes. They gave no interpretation either of the fact that, in contrast to the quaternary ammonium complexes, these diphenyliodonium compounds start to decompose exothermally, nor of the fact that, at the beginning of the thermal decomposition of diphenyliodonium complexes, the formation of PhCN prevails. In addition, they gave no data on the PhI : PhCN ratio in the gaseous product or on the nature of final decomposition product.

The incompleteness of these data led us to investigate the thermal decomposition of cyano complexes with various onium cations. The known types of onium cations and the binary cyano complexes with onium cations that have been prepared are presented in Table 1.

The thermal properties of the cyano complex compounds prepared by us were investigated by using the TG/DTG and DTA techniques with a Derivatograph. In order to complete our data, we also used less traditional techniques such as EGA, DSC and ETA measurements in vacuo together with thermogravimetry, mass spectroscopy, infra-red (IR) spectroscopy and, in the case of iron compounds, Mössbauer spectroscopy.

We have prepared and investigated more than 90 new cyano complex compounds containing tertiary sulphonium, tertiary telluronium or secondary iodonium cations. We worked out the methods of their preparation and identified all the compounds by chemical analysis and IR spectroscopy.

EXPERIMENTAL

Methods of measurement

The thermal decomposition of all prepared compounds was studied using the Derivatograph device (MOM, Hungary) in TG/DTG and DTA modes

in a dynamic inert-gas atmosphere (argon and nitrogen) in a platinum crucible. α-Al_2O_3 was used as the reference sample. The sample mass was 100 mg, the sensitivities of TG, DTA and DTG were 100 or 50 mg, 1/10 and 1/15, respectively. The heating rate was 5 to 10 K min^{-1}.

The IR absorption spectra of the starting solid compounds, and the intermediate and final products of the thermal decomposition were recorded on a Specord (Model 80, Jena, Germany) in KBr pellets (5 mg of sample per 500 mg KBr) in the range 4000–200 cm^{-1}. The gaseous reaction products were condensed and their IR spectra in CH_2Cl_2 were measured.

The ETA of the starting samples and of the decomposition intermediates was performed using the ETA device of the Nuclear Research Institute (Řež, Czechoslovakia). The sample mass was 100 mg and the heating and cooling rates were 5 and 2.5 K min^{-1}, respectively. Argon atmosphere and corundum crucibles were used. The Rn emanation rate is given in relative units.

The compounds prepared and the intermediate and final products of their thermal decomposition were identified by elemental analysis (CHN analyzer, Hewlett-Packard) and by chemical analysis.

The radiation source used for the Mössbauer spectroscopy was ^{57}Co diffused in platinum. The measurements were performed under cooling with liquid nitrogen. $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ was used for calibration. The isomeric shift related to α-iron was taken into account.

Preparation of compounds

Synthesis of compounds

Cyano complexes of the general formula $A_x[M(CN)_y]$, $A_x[M(CN)_5L]$ and $A_x[M(CN)_4L_2]$, where $A = [R_4N]^+$, $[Me_3S]^+$, $[Me_2PhS]^+$, $[Ph_3S]^+$, $[Ph_3Te]^+$ or $[Ph_2I]^+$, $L = NO$, PPh_3, NH_3, dipy or phen, $M = Cu$, Ag, Au, Zn, Cd, Hg, Ni, Pd, Pt, Fe, Co, Ni, Mn, Cr, Mo or W, $x = 1$, 2, 3 or 4 and $y = 2$, 3, 4, 6 or 8 were prepared by means of the reactions described below.

Compounds containing a secondary iodonium cation

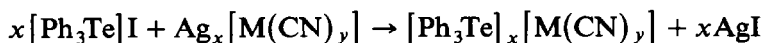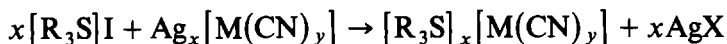$$x Ph_2ICl + K_x[M(CN)_y] \rightarrow [Ph_2I]_x[M(CN)_y] + x KCl$$
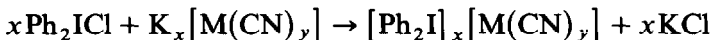
The crystals of the cyano complex with the diphenyliodonium cation were prepared by adding the stoichiometric quantity of the respective alkali cyano complex to the saturated aqueous solution of Ph_2ICl at 50°C with intense stirring for 30 min, followed by a continuous cooling of the reaction mixture. The product was separated using a S-3 sintered glass filter, washed with alcohol and dried in vacuo. The recrystallization was done using an aqueous alcohol solution [9].
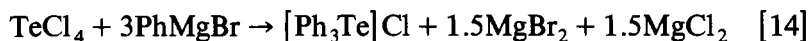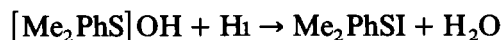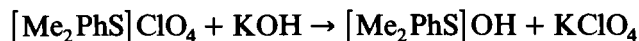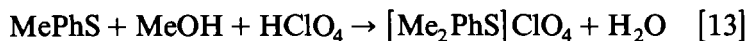
Ph_2ICl was prepared according to the method described by Beringer et al. [10]

$$KIO_3 + 2C_6H_6 + 2(CH_3CO)_2O + 2H_2SO_4$$
$$\rightarrow [(C_6H_5)_2I]HSO_4 + KHSO_4 + 4CH_3COOH + 0.5O_2$$
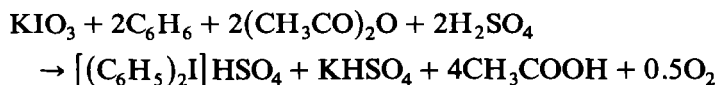
Compounds containing a tertiary sulphonium cation and a telluronium cation

$$x[R_3S]I + Ag_x[M(CN)_y] \rightarrow [R_3S]_x[M(CN)_y] + xAgX$$

$$x[Ph_3Te]I + Ag_x[M(CN)_y] \rightarrow [Ph_3Te]_x[M(CN)_y] + xAgI$$

First, a compound containing a tertiary onium cation (Me_3SI, Me_2PhSI, Ph_3SBr, Ph_3SI or Ph_3TeI) was prepared in the following way:

$$Me_2S + MeI \rightarrow Me_3SI \quad [11]$$

$$Ph_2SO + PhMgBr \rightarrow [Ph_3S]OMgBr \xrightarrow{2HBr} [Ph_3S]Br + MgBr_2 + H_2O \quad [12]$$

$$MePhS + MeOH + HClO_4 \rightarrow [Me_2PhS]ClO_4 + H_2O \quad [13]$$

$$[Me_2PhS]ClO_4 + KOH \rightarrow [Me_2PhS]OH + KClO_4$$

$$[Me_2PhS]OH + HI \rightarrow Me_2PhSI + H_2O$$

$$TeCl_4 + 3PhMgBr \rightarrow [Ph_3Te]Cl + 1.5MgBr_2 + 1.5MgCl_2 \quad [14]$$
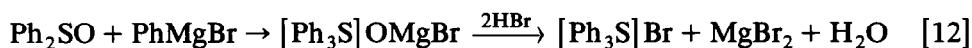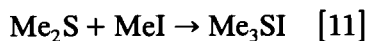
The cyano complex compounds with the cations $[Me_3S]^+$, $[Me_2PhS]^+$, $[Ph_3S]^+$ and $[Ph_3Te]^+$ were prepared by adding the stoichiometric quantity of an aqueous solution of the compound with the tertiary sulphonium or telluronium cation to the calculated amount of the aqueous suspension of the silver salt of the cyano complex. The reaction was allowed to proceed for 1 h under intense stirring. After the formation of the yellow precipitate of AgI, the reaction mixture was filtered and the filtrate condensed by evaporation. By continuous cooling the desired products crystallized; the recrystallization was performed from an alcohol/ether solution. The product was dried in vacuo [15].

The cyano complex compounds with the $[R_4N]^+$ cation were prepared according to Mohai and Bagyin [6], and those with the alkali cation according to Sharpe [16].

Preparation of samples for ETA measurements

The samples for ETA measurements were prepared by labelling the compounds in the surface by the adsorption of the nuclides [228]Th or [224]Ra from acetone solution. Prior to the measurement, the samples were stored for at least 4 weeks. [220]Rh atoms are formed by spontaneous radioactive decay according to the scheme

$$^{228}Th \rightarrow {}^{224}Ra \rightarrow {}^{220}Rn$$
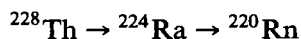
RESULTS AND DISCUSSION

DTA, TG, DTG analyses and Mössbauer and IR spectroscopies

The results of the thermal analysis were obtained in the form of diagrams. The thermal properties were investigated using four groups of compounds

TABLE 2

Decomposition temperature ($^\circ$C) of diamagnetic cyano complexes according to the type of cation

Cation	Anion		
	$[Fe(CN)_5NO]^{2-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$
$[Me_4N]^+$	300	300	370
$[R_4P]^+$	≈ 260	≈ 280	≈ 345
$[Ph_3S]^+$	225 (Sec r)	275	300, 350
$(NH_4)^+$	220 (Sec r)	200	330
$[Me_3S]^+$	240	150, 190	200, 280
Ph_3Te^+		230	
H^+	175	190	225
$[Ph_2I]^+$	150, 190	155	215

Sec.r mean $Ph_2S + NO \rightarrow Ph_2SO + \frac{1}{2}N_2$, $\frac{2}{3}NH_3 + NO \rightarrow H_2O + \frac{5}{6}N_2$

(those containing the $[R_4N]^+$, $[R_3S]^+$, $[R_3Te]^+$ or $[Ph_2I]^+$ cation) under identical and reproducible experimental conditions. A more complex investigation of these compounds led to the following conclusions.

(1) Cyano complexes with the $[R_4N]^+$ cation are of explicitly ionic character. A gradual shift to covalent character is observed with the compounds containing the tertiary sulphonium cation, followed by the secondary iodonium compounds. The thermal stability of these compounds is also connected with this character. Table 2 shows the initial temperature of the decomposition of some diamagnetic cyano complexes as a function of the type of cation. It can be seen from these data that, in agreement with the ionic character, the quaternary ammonium cyano complexes are in all cases decomposed at the highest temperature, whereas the secondary iodonium compounds decompose at the lowest temperature. The compounds with the $[R_4P]^+$ and H^+ cations decompose at intermediate temperatures. Table 2 also shows the fact that protonated cyano complexes exhibit a higher thermal stability than the corresponding diphenyliodonium cyano complex. The compounds $[Ph_3S]_2[Fe(CN)_5NO]$ and $[NH_4]_2[Fe(CN)_5NO]$ represent an exception; they decompose at lower temperatures than expected. This effect is caused by the oxidation of the NO ligand in a secondary reaction with Ph_2S or NH_3, evolved from the cation under the formation of Ph_2SO and N_2, and H_2O and N_2, respectively. The strongly exothermic character of the process results in the lower decomposition temperature (see Fig. 1(d)).

(2) The cyano complexes containing the $[Ph_3S]^+$ cation exhibit a higher thermal stability than do compounds containing the $[Me_3S]^+$ cation (Fig. 1(a) and 1(c)). This is related to the electronic structure of the sulphonium cation [15]. In the $[Me_3S]^+$ cation the methyl groups are in the tetrahedral configuration and are bonded to the S atom by a σ bond, whereas in the
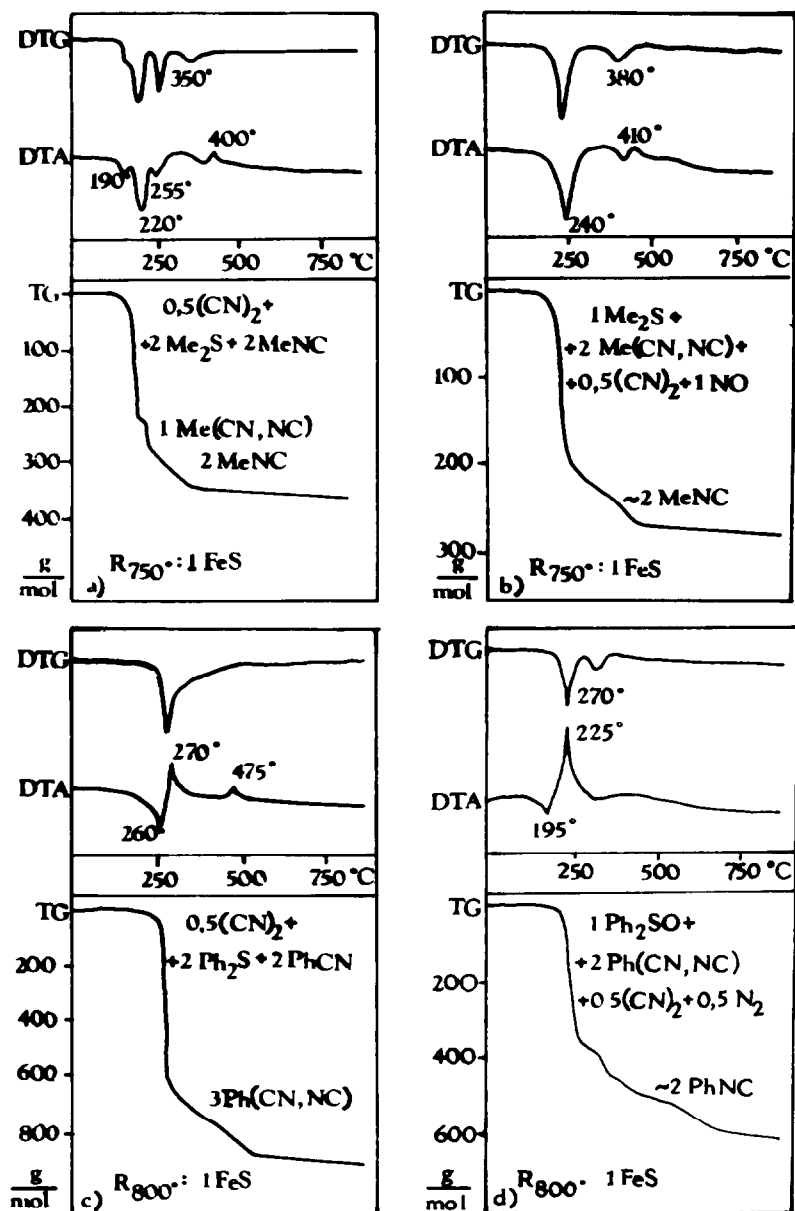
Fig 1 TG, DTG and DTA curves of $[R_3S]^+$ iron cyano complexes. (a) $[Me_3S]_3[Fe(CN)_6]$, (b) $[Me_3S]_2[Fe(CN)_5NO]$, (c) $[Ph_3S]_3[Fe(CN)_6]$, (d) $[Ph_3S]_2[Fe(CN)_5NO]$

$[Ph_3S]^+$ cation a $p^\pi-d^\pi$ bond is formed between the phenyl groups and the S atom. This causes a strengthening of the interaction between the central atom and the ligand: the form of the $[Ph_3S]^+$ cation is shifted from the tetrahedral structure to a trigonal planar one.

When the sulphonium cation is decomposed at a lower temperature than the anion of the cyano complex, the methyl groups split off cyanide ligands
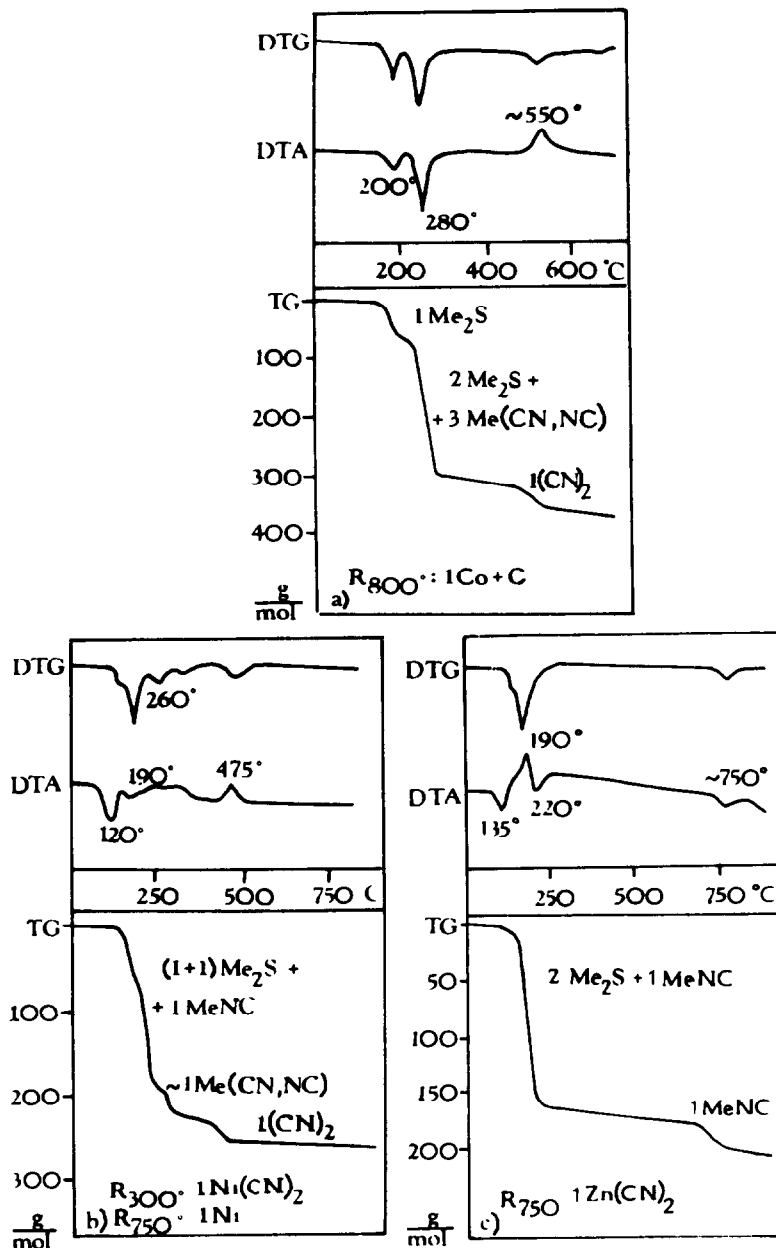
Fig. 2 TG, DTG and DTA curves of: (a) $[Me_3S]_3[Co(CN)_6]$; (b) $[Me_3S]_2[Ni(CN)_4]$; (c) $[Me_3S]_2[Zn(CN)_4]$.

in an endothermic reaction and, besides Me_2S, MeNC is also formed at the beginning of the reaction (Fig. 2(b) and 2(c)). In the case where the methyl groups split off at such a temperature that the cyano complex anion is also decomposed, MeCN/NC is formed simultaneously (Fig. 1(b)). From the
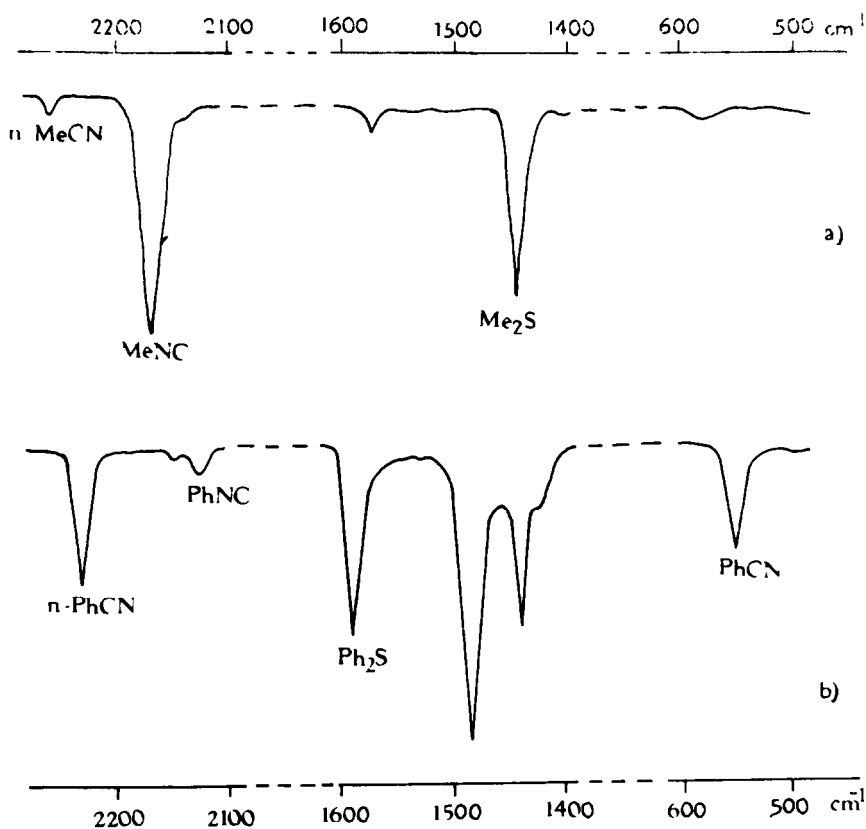
Fig. 3. IR absorption spectra of the gaseous decomposition products of (a) [Me$_3$S]$_3$[Fe(CN)$_6$] at 225°C, (b) [Ph$_3$S]$_3$[Fe(CN)$_6$] at 275°C

compounds with the [Ph$_3$S]$^+$ cation, PhCN or PhCN/NC is evolved at the beginning of the decomposition. Phenyl groups split off at a higher temperature during the melting of the complex. Besides Ph$_2$S, PhCN is also formed in the first decomposition step. PhNC is formed at a higher temperature in an exothermic process and is only released afterwards (Fig. 1(d)). This process is evidenced by the IR spectra (Fig. 3). In the case where the ratio of the evolved sulphide and cyanide components is equal to 1, the elemental metal is formed via its cyanide. When this ratio is lower than 1, the metal sulphide is formed. Compounds containing the [Me$_2$PhS]$^+$ cation exhibit properties intermediate between those exhibited by compounds containing the [Me$_3$S]$^+$ and [Ph$_3$S]$^+$ cations.

(3) The compounds containing the diphenyliodonium cation start to decompose in an exothermic process (Fig. 4). The higher the portion of PhI that splits off without PhCN, the more exothermic is the process. This is due to the fact that the mutual interaction between the cation and the anion in diphenyliodonium cyano complexes takes place in the solid state [17,18]. This interaction is also evidenced by the shift in the ν(CN) values towards
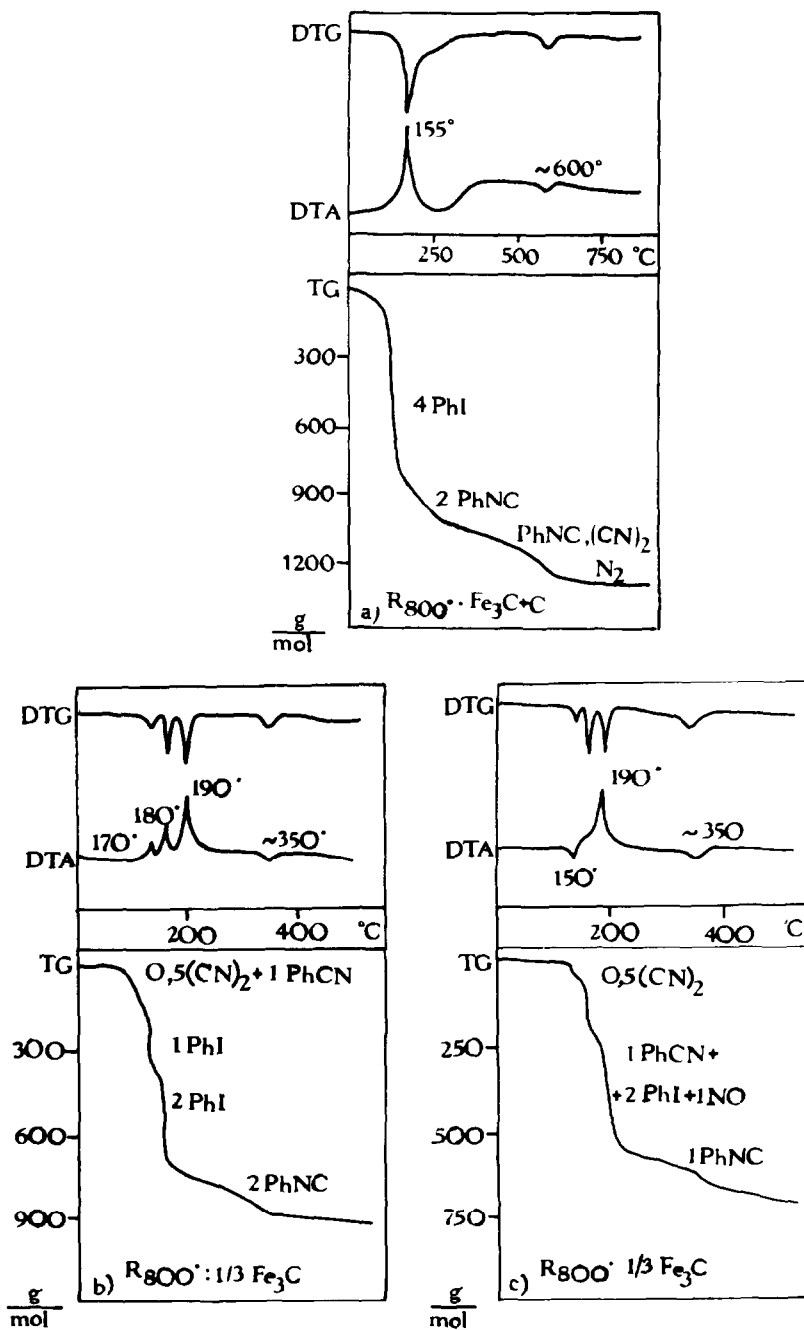
Fig 4 TG, DTG and DTA curves of $[Ph_2I]^+$ iron cyano complexes (a) $[Ph_2I]_4[Fe(CN)_6]$, (b) $[Ph_2I]_3[Fe(CN)_6]$, (c) $[Ph_2I]_2[Fe(CN)_5NO]$.

lower wavenumbers in comparison with the alkali cyano complex (Table 3). Even more pronounced is the shift of $\nu(NO)$ towards lower wavenumbers. The compound $[Ph_2I]_4[Fe(CN)_6]$ is an exception, due to the asymmetric

TABLE 3

The stretching vibrations (in cm^{-1}) ν(CN) and ν(NO) according to the type of cation in the complex

Cation	Anion				
	$[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Fe(CN)_5NO]^{2-}$	
Na$^+$, K$^+$	2130–2145	2115–2130	2040–2050	2145–2180	1945
[Me$_4$N]$^+$	2120	2105–2110	2030–2045	2136	1920
[Bu$_4$N]$^+$	2110	2100	–	2135	1885
[Me$_3$S]$^+$	2130	2105	2045	2135	1925
[Ph$_3$S]$^+$	2135	2120	2050	2140	1895
[Ph$_2$I]$^+$	2110, 2125	2095, 2110	2090(^{1})	2125	1890
(NH$_4$)$^+$	2130	(2035), 2120	(2030), 2043(2070)	2140–2145	1940
H$^+$	2130, 2204	2077, 2100	(2030)	2145	
		2125	2077, 2100	2175–2200	1950

configuration of the [Ph$_2$I]$^+$ ions which results in a strong quadrupole splitting (Table 4). The high value of ν(CN) is also a result of this asymmetric configuration [19]. As the [Ph$_2$I]$^+$ group exhibits an electron-acceptor effect on the central atom, Fe seems here to be trivalent rather than divalent.

The shift of the ν(CN) values towards lower wavenumbers in comparison with the alkali cyano complex can be explained by the increase in the mutual interaction Ph $\cdots$ NC. The lower the ν(CN) value, the lower the temperature of the exothermic reaction. With a shift in the ν(CN) values towards higher wavenumbers, the thermal stability of the compounds is increased (Table 5). The compound [Ph$_2$I]$_2$[Fe(CN)$_5$NO] represents an

TABLE 4

IR and Mossbauer spectroscopic data for the iron hexacyano complexes

Compound	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	ν(CN) (cm^{-1})
K$_4$[Fe(CN)$_6$] 3H$_2$O	−0 35	0	(2030), 2045, 2075, (2095)
[Me$_3$S]$_4$[Fe(CN)$_6$]	−0 35	0	(2030), 2045, (2060), (2075)
[Ph$_3$S]$_4$[Fe(CN)$_6$]	−0.29	~ 0.15	(2030), 2050, (2065), (2080)
[Ph$_2$I]$_4$[Fe(CN)$_6$]	−0 39	1 10	2070, 2090, 2105, (2115)
[Ph$_2$I]$_2$H$_2$[Fe(CN)$_6$]	−0.55	0	(2015), 2045, 2085
H$_4$[Fe(CN)$_6$]	−0 48	0	2075, 2100
K$_3$[Fe(CN)$_6$]	−0 45	0 28	(2080–2090), 2120–2130
[Me$_3$S]$_3$[Fe(CN)$_6$]	−0 41	0 55	2025, 2060, 2105
[Ph$_3$S]$_3$[Fe(CN)$_6$]	−0 43	0 65	2100, 2120, 2130
[Ph$_2$I]$_3$[Fe(CN)$_6$]·3H$_2$O	−0 45	1.51	2095, 2100, 2110, (2120)
H$_3$[Fe(CN)$_6$]	−0 32	0 46	2077, 2100, 2120

TABLE 5

Stretching vibrations ν(CN) and initial decomposition temperatures of $[Ph_2I]^+$ cyano complexes

Compound	ν(CN) (cm^{-1})	T ($^\circ$C)
$[Ph_2I]_3[Fe^{II}(CN)_5PPh_3]$	2050	90
$[Ph_2I]_3[Fe^{II}(CN)_5PBu_3]$	2065	100
$[Ph_2I]_3[Mn(CN)_5NO]$	2080, (2090), (2105), 2135	105
$[Ph_2I]_3[Mn(CN)_6]$	2085, (2105), 2115, (2120)	140
$[Ph_2I]_4[Fe^{II}(CN)_6]$	2070, 2090, 2105, (2115)	155
$[Ph_2I]_3[Cr(CN)_5NO]$	2095, (2100), 2115, 2130	190
$[Ph_2I]_3[Cr(CN)_6]$	2110, (2115), 2120, 2135	200
$[Ph_2I]_3[Co(CN)_6]$	2110, 2125, 2140	215

exception: the ν(CN) values are higher than those corresponding to the decomposition temperature as the NO group is a better π acceptor than is the CN group. The stronger mutual interaction between NO and Ph is inferred from the fact that NO splits off only after the release of $(CN)_2$.

(4) The changes in the morphology of the solid cyano complex compounds were investigated by means of ETA. During the course of the thermal decomposition of some cyano complex compounds, reversible endothermic processes and irreversible exothermic processes are observed prior to melting. Evidence for the existence of these changes was obtained by ETA.

On the DTA curve of $[Ph_2I]_3[Cr(CN)_5NO]$ (Fig. 5) two exothermic irreversible effects at 65 and 110°C appear prior to the thermal decomposition. When the IR spectrum of the original compound at 20°C is compared with that of the sample previously heated to 80°C (a temperature above that of the first exothermic effect), no changes in the intensity or position of the absorption bands corresponding to the stretching vibrations ν(CN) and ν(NC) were observed. However, when the compound was heated up to 125°C (i.e. above the second exothermic effect), the absorption band corresponding to the stretching vibrations ν(CN) and ν(NO) that was originally split is changed into a singlet (Fig. 6). This is probably caused by the stabilization of the system after the release of energy (the exothermic process at 110°C) and by the increase in the molecular symmetry. The thermal decomposition starts with the evolution of PhI and PhCN (the exothermic process at 190°C). At higher temperatures the NO ligand, which does not enter the secondary reaction, splits off, in contrast to some cyano complex compounds with the coordinated NO group [15]. The gaseous and the solid decomposition products were both identified using IR spectroscopy. Cr_3C_2 is the final product of the decomposition.

The results of the ETA obtained for the compound $[Ph_2I]_3[Cr(CN)_5NO]$ are presented in Fig. 5. In the temperature range 20–180°C no decomposi-
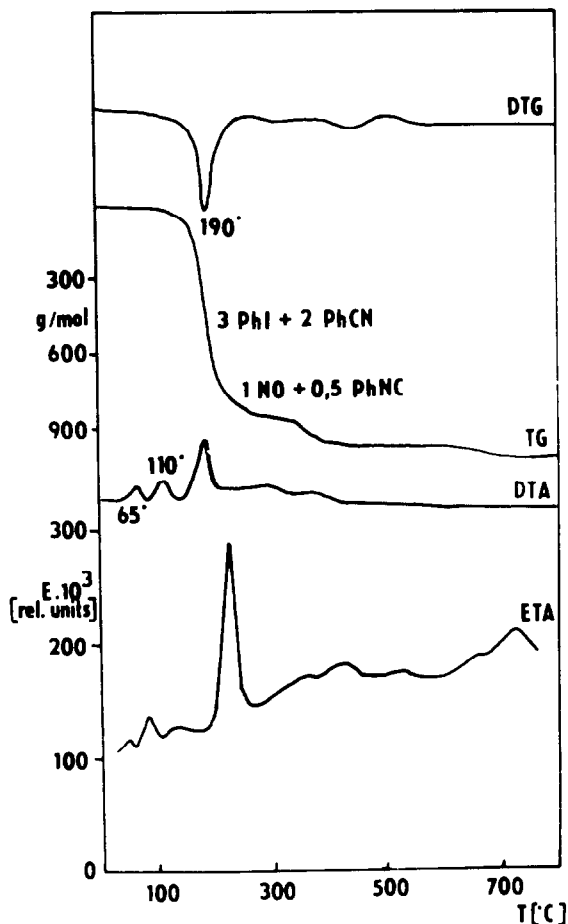
Fig. 5. TG, DTG, DTA and ETA curves of $[Ph_2I]_3[Cr(CN)_5NO]$.

tion of the sample is observed. Above $50°C$, the emanation rate increases; the following decreases in this rate at $65°C$ and $110°C$ correspond to the exothermic effects seen on the DTA curve. This process is irreversible; these effects did not reappear on either the DTA or the ETA curves when the sample was reheated. On further heating a pronounced increase in the emanation rate on the ETA curve was observed, followed by an instantaneous decrease at $220°C$, corresponding to the evolution of 3 PhI and 2 PhCN (according to the TG curve). On further heating to $400°C$, NO and PhNC are released from the molecule. These chemical processes show no significant effects on the ETA curve. We may suppose that, during the evolution of the gaseous decomposition products, the texture (morphology) of the sample is transformed. The value of the emanation rate may found on heating above $400°C$ supports the conclusions drawn about the texture configuration of the final product (Cr_3C_2). When heated above $700°C$ the sample sinters. The ETA curves recorded during the slow cooling of the
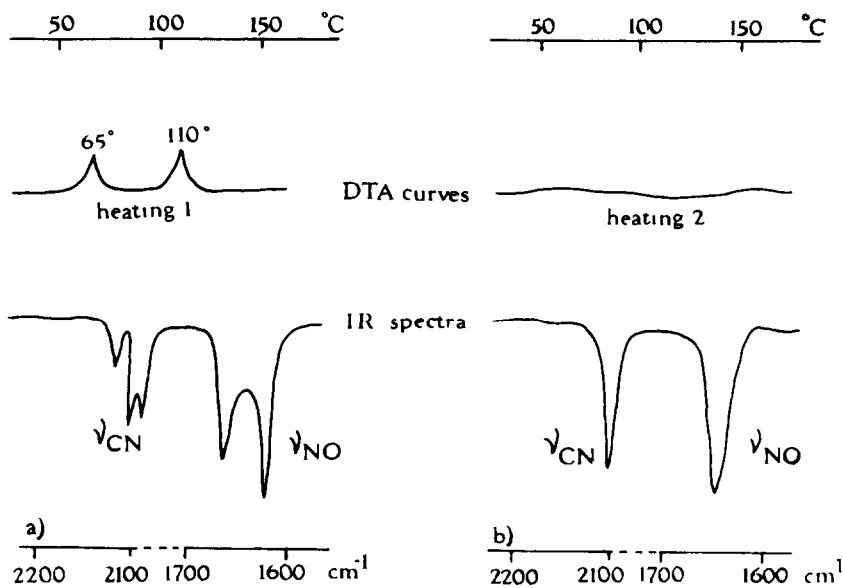
Fig 6 Irreversible exothermic effects and IR spectra of the thermal decomposition of [Ph$_2$I]$_3$[Cr(CN)$_5$NO] (a) before heating, (b) after heating to 125°C.

intermediate decomposition products, prepared by prior heating to either 250°C or 650°C, exhibit properties typical of highly dispersed organic materials with a high diffusion coefficient for radon, whereas in the case of the final product obtained by heating to 780°C the ETA curve is exponential in character, which is typical of inorganic materials having a substantially lower diffusion coefficient for radon.

On the basis of the ETA cooling curve obtained for this sample after its non-isothermal heating in argon atmosphere, the curve of log E vs. $1/T$ was plotted. The activation energy of radon diffusion, $E_D = 60$ kJ mol^{-1} was calculated for the temperature range 500–720°C (where the diffusion within the sample is not influenced by sintering). The final decomposition product (Cr$_3$C$_2$ + C according to TG) is characterized by a very high degree of structural disorder.

CONCLUSIONS

The thermal decomposition of the solid cyano complexes of the first and second-row transition depends on the type of cation and the nature of central atom, with different intramolecular reactions taking place during the course of the decomposition. We have explained the cause of the formation of cyanide and isocyanide for a large group of compounds.

We found that in the course of heating some of these compounds, isophase transformation, sintering and morphological changes take place, which are sensitively indicated by the ETA technique. This technique

allowed us to characterize the diffusion properties of the thermal decomposition products of the complex compounds. When complex compounds having a central metal atom are used as starting materials for the preparation of very pure and highly reactive metals, ETA may represent a very useful technique. This method may be used to characterize the reactivity of highly dispersed metals prepared in this way as well as for evaluating their degree of structural order. This is important mainly in the application of these compounds as catalysts, etc.

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