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THERMAL STABILITY OF TRIMETHYL AND TRIPHENYL SULFONIUM CYANO METALLATES OF THE $[M(CN)_5NO]^{3-}$ TYPE

Katarína Györyová, P.J.Šafarik's University
Košice, Czechoslovakia
Béla Mohai, Technical University
Veszprém, Hungary

ABSTRACT

Some complexes of the $[M(CN)_5NO]^{3-}$ type (M = Cr, Mn) with $[Me_3S]^+$ and $[Ph_3S]^+$ "onium" cations were prepared and their thermal decomposition was investigated by the non-isothermal method in order to elucidate the mechanism of decomposition and the character of decomposition products.

INTRODUCTION

The investigation of thermal decomposition of different cyano complexes with secondary $[Ph_2I]^+$ and tertiary $[R_3S]^+$ "onium" cation /1,2/ is a continuation of previous studies dealing with the thermal decomposition of quaternary ammonium cyano complexes /3,4/. In contrast to very soluble quaternary ammonium compounds, these cyano complexes are more likely to exhibit a covalent character. It results from this property that the thermal stability of cyano complexes with "onium" cations decreases in this order: $R_4N^+ > R_3S^+ > R_2I^+$ /5/. We have found that an interaction between the "onium" cation and the cyano complex anion depending on the type of anion takes place in the thermal decomposition and significantly affects the mechanism of this decomposition. In order to clear up these interactions, we synthetized a few cyano complexes compounds with mixed ligands of the type $[M(CN)_5NO]^{3-}$ and investigated the interaction of the ligands released during the thermal decomposition with the $[R_3S]^+$ cations.

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MEASURING METHODS

The thermal decomposition of the synthetized substances was performed in a Derivatograph MOM OD 102 in a platinum crucible and argon atmosphere at temperatures up to 900°C. The rate of heating was $10^{\circ}C\ min^{-1}$, DTA sensibility 1/5, DTG sensibility 1/10 and Al_2O_3 was used as a reference substance.

The volatile decomposition products were collected and analyzed in a separate experiment. These decomposition products were identified by chemical analysis and infrared spectroscopy.

The infrared spectra were recorded with a spectrophotometer Perkin Elmer Model 577. The KBr and CsI disc technique was used in the spectral range 4000-200 cm^{-1} calibrated by means of polystyrene.

RESULTS AND DISCUSSION

We prepared three new cyano complex compounds, i.e. $[Ph_3S]_3[Mn(CN)_5NO]$, $[Me_3S]_3[Mn(CN)_5NO]$, and $[Me_3S]_3[Cr(CN)_5NO]$ by the reaction of the silver salt of cyano complex with a compound Me_3SI or Ph_3SI, containing tertiary sulfonium cation. This preparation is analogous to the preparation described in our foregoing publication /6/. The formed complex compound can be separated from the solution by crystallization.

The comparison of the thermal decompositions of these compounds indicates that the compounds containing the $[Me_3S]^+$ cations are least stable. That is due to different electron structure of the sulfonium cations. Whereas the Me groups tetrahedrally ordered in the $[Me_3S]^+$ cation are bonded to sulfur only by a 1 π-bond, $p\widetilde{\pi} - d\widetilde{\pi}$ -bonds come into existence between the π- electrons of phenyl ligands and the d-orbitals of sulfur in the $[Ph_3S]^+$ cation. Owing to this fact, the bond between the central atom and ligand becomes stronger and the phenyl groups are split off at higher temperature. The Ph-NC bonds get more stable in the exothermic effect and subsequently PhNC is released.

As for compounds $[Ph_3S]_3[Mn(CN)_5NO]$ and $[Me_3S]_3[Cr(CN)_5NO]$, a secondary reaction takes place between the liberated NO ligand and Ph_2S or Me_2S arising from the cation to give sulfoxides:

$$Ph_2S + NO \longrightarrow Ph_2SO + \frac{1}{2} N_2$$

$$Me_2S + NO \longrightarrow Me_2SO + \frac{1}{2} N_2$$

which manifests itself on the DTA curve by a vigorous exothermic reaction while the NO ligand coming from $[Me_3S]_3[Mn(CN)_5NO]$ has no oxidative effect and is liberated unchanged.

Whether the NO group reacts with the present ligands depends on the character of the products of splitting (decomposition). We have found that the lower is the value of ν_{NO}, the more capable is NO to undergo a nucleophilic oxidation (for the first compound ν_{NO} = 1700 cm^{-1} and for the second one ν_{NO} = 1645 cm^{-1}). The compounds $[Ph_3S]_2[Fe(CN)_5NO]$ and $(NH_4)_2[Fe(CN)_5NO]$ which were investigated earlier /6/ are subjected to similar nucleophilic oxidation.

This oxidation does not appear with $[Me_3S]_3[Mn(CN)_5NO]$ because the NO ligand has no oxidation effect on the cation. Because of a high ν_{NO} value of the NO group, this ligand does not undergo a nucleophilic oxidation even in the case of the compounds $[Me_3S]_2[Fe(CN)_5NO]$, $[Ph_2I]_2[Fe(CN)_5NO]$, $[Ph_2I]_3[Cr(NO)_5NO]$ and $[Ph_2I]_3[Mn(CN)_5NO]$ where no secondary reaction proceeds /6,7/.

CONCLUSIONS

An interaction between the "onium cation" and the cyano complex anion depending on the type of anion and cation appears during the thermal decomposition of $[Ph_3S]_3[Mn(CN)_5NO]$, $[Me_3S]_3[Mn(CN)_5NO]$ and $[Me_3S]_3[Cr(CN)_5NO]$ and significantly affects the mechanism of decomposition.

At low values of ν_{NO} the NO ligand oxidizes the liberated gaseous decomposition products and Ph_2SO or Me_2SO arises. N_2, MeCN, PhNC, PhCN, Mn_3C, MnS, and $Cr(CN)_2$ are also formed in the course of this thermal decomposition. The thermal decomposition of these compounds has been compared with the thermal decomposition of the previously studied cyano complex compounds containing the $[Ph_2I]^+$ cation /7,8/.

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