Thermochimica Acta, 93 (1985) 97-100
Elsevier Science Publishers B.V., Amsterdam

THERMOANALYTICAL STUDY OF PICOLINE COMPLEXES

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ABSTRACT

The thermal behaviour of transition-metal halide complexes formed with picoline was studied by derivatograph. The thermal decomposition of the complexes can take place either in molten or in solid phase in several steps. The mechanism of the stepwise reaction was also investigated.

INTRODUCTION

The transition-metal halide complexes formed with pyridine and its derivatives have been extensively studied and several investigations have been reported about their thermal properties. The transition-metal picoline halides have proved to be suitable models for investigating of thermal behaviour of complex compounds. These complexes can form clathrates with a number of organic compounds so they obtained some industrial importance.

In our previous works we studied the thermal properties of a number of pyridine [1] and some picoline complexes [2]. Now we present our results of the thermoanalytical and different other analytical measurements obtained in connection transition-metal picoline halides.

The following complexes were prepareted:

ML_nX_2	Ni	Co	Mn	Cd	Cu	Zn	
	2	2*	1	1	2*	2*	α-pic
Cl	4	4	4	2	2	2*	β-pic
	4	4	4	4	2,5	2*	γ-pic
	2*	2*	1	2	2*	2*	α-pic
Br	4	4*	4	2	2	2*	β-pic
	4	4*	4	4	4	2*	γ-pic
	1*	2*	1	2*	-	2*	α-pic
I	4	4*	4*	2*		2*	β-pic
	6	4*	4*	4*		2*	γ-pic

Proceedings of ICTA 85, Bratislava

EXPERIMENTAL

The compounds were prepared by dissolving metal-halide and picoline in a solvent and by refluxing the solution for 1-2 hours. The solvents were picoline, water, methanol, ethanol and acetone. The products are solid.

The thermoanalytical measurements were carried out by derivatograph. Some other analytical methods (X-ray, IR, far-IR) were applied to investigate the crystalline and molecule structure of the complexes.

RESULTS

The thermoanalytical investigations indicated the complexes to put into two groups on the basis of their thermal properties:

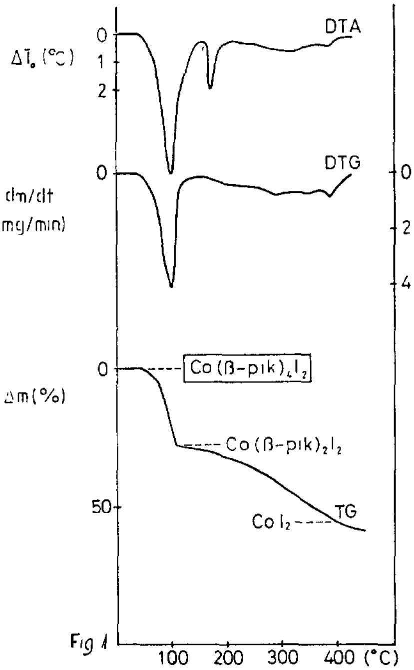

Fig 1

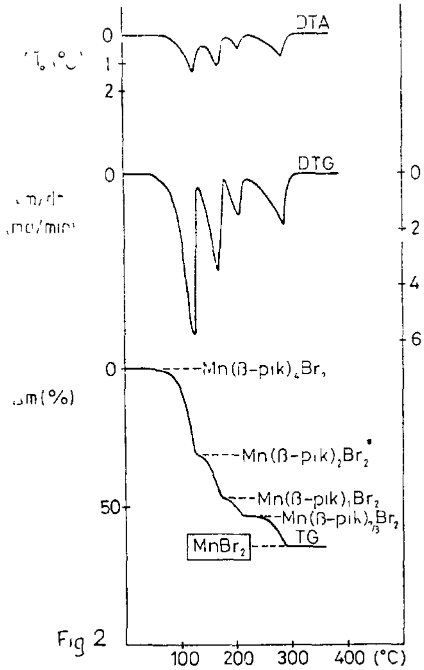

Fig 2

A. Thermal decomposition in molten phase

Derivatogram of Co(β-pik)$_4$I$_2$ is shown in Fig.1. Two decomposition steps are indicated by the TG- and DTG-curves. The second DTA-peak is supposed to be in connection with the melting of the sample, observed by thermomicroscope too. Therefore the first decomposition step takes place in solid phase and the second one is characterized by a spinned out DTG-curve in molten phase.

It is worth while to mention that all of the Zn-complexes contain two ligands and their decomposition takes place also in molten phase.

The thermal decomposition of the first group of complexes (marked with an asterisk in Table) proceeds on the same way characterized by the following equations:

ML_4X_2 (s) $\longrightarrow$ ML_2X_2(s) + 2 L(g)

ML_2X_2 (s) $\longrightarrow$ ML_2X_2(l)

ML_2X_2 (l) $\longrightarrow$ MX_2 + 2L(g)

B. Thermal decomposition in solid phase

The other group of the complexes, including the $Mn(\beta\text{-pic})_4Br_2$ shown in Fig.2 exhibits stepwise thermal decomposition process occuring in solid phase.

As it can be seen in Fig. 2 the whole process consists of four steps, all of them result well defined intermediates of stoichiometric composition. Polynucleare structure must be attributed to the compounds of the overall formula $ML_{2/3}X_2$.

The stepwise thermal decomposition of the complexes is to be described by the following equations:

ML_4X_2 (s) $\longrightarrow$ ML_2X_2(s) + 2L(g)

ML_2X_2 (s) $\longrightarrow$ ML_1X_2(s) + L(g)

ML_1X_2 (s) $\longrightarrow$ $ML_{2/3}X_2$(s) + 1/3 L(g)

$ML_{2/3}X_2$ (s) $\longrightarrow$ MX_2(s) + 2/3 L(g)

The intermediates can not be prepared from solution. Their isolation is possible only by the means of derivatograph freezing the thermal decomposition at the appropriate temperature.

We intended to get information about the mechanism of thermal decomposition by studying the structure of the intermediates. The Mn-complexes were analysed by applying X-ray powder diffraction, IR, far-IR spectroscopy and magnetic momentum measurements.

The following results were obtained:

- All the intermediates are crystallines with monoclinic or orthorombic lattice cells.

- The complexes of four ligands is to be characterized by octahedral structure with trans Mn-X bonds.
- The main group of intermediates with two ligands has tetrahedral structure.
- All of the other intermediates have polymeric structure containing Mn-halide-Mn (Mn-X-Mn) bridges.

We obtained information about the mechanism of the step by step thermal decomposition knowing the molecule structure of the intermediates.

The reaction steps are in connection with dissotiation except the case, in that an intermediate with M-X-M bridges is formed. This process is to be regarded to substitution, because of splitting a bond and of forming a new one at the same time.

CONCLUSIONS

The thermal decomposition of transitional-metal picoline halides takes place either in molten phase or in solid phase by concsecutive reactions. The solid phase mechanism occures if the complex has inclination to form intermediates with M-X-M bridges. The probability of M-X-M bridge formation is the higher the greater is the electron density in the halide.

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