Monatshefte für Chemie 129, 473–480 (1998)

Monatshefte für Chemie
Chemical Monthly

Thermal Properties of Metal Derivatives of 6-Aminopicolinic Acid

B. Kowalczyk[1,*], **W. Baran**[2], and **K. Chaczatrian**[2]

[1] Institute of Chemistry, Pedagogical University, PL-42200 Częstochowa, Poland
[2] Department of Chemistry, H. Kołłątaj Academy of Agriculture, PL-30015 Kraków, Poland

Summary. The thermal decomposition of Mn(II), Cr(III), and Pb(II) salts of 6-aminopicolinic acid (*AP*H) has been studied up to 1200°C in air and in helium atmosphere. Decomposition processes are proposed, and the resulting mass losses are compared with those obtained from experimental data. The analysis of solid decomposition products was carried out using X-ray diffractometric methods. The compounds decompose thermally to metal oxides. The samples have also been investigated by DSC in nitrogen atmosphere in the temperature range of 20–550°C. The values of the transition enthalpy were determined.

Keywords. Decomposition; X-Ray diffraction; DSC; Enthalpy.

Thermische Eigenschaften von Metallderivaten von 6-Amino-2-pyridincarbonsäure

Zusammenfassung. Die thermische Zersetzung der Mn(II)-, Cr(III)- und Pb(II)-Salze von 6-Amino-2-pyridincarbonsäure (6-Aminopicolinsäure, *AP*H) in Luft und in Helium wurde bis 1200°C untersucht. Reaktionswege werden vorgeschlagen, und die sich daraus ergebenden theoretischen Masseverluste werden mit experimentellen Daten verglichen. Die Analyse der festen Zersetzungsprodukte erfolgte mittels Röntgendiffraktionsmethoden. Die Verbindungen gehen beim Erhitzen in Metalloxide über. Die Übergangsenthalpien der Salze wurden mittels DSC von 20–550°C in einer Stickstoffatmosphäre bestimmt.

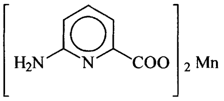
Introduction

The syntheses and structures of metal derivatives of 6-aminopicolinic acid (*AP*H) along with their elemental analyses and IR spectra have been reported previously [1]. According to an IR study based on the *Gill* criterion [2], all metal derivatives except those of copper are *AP*H salts. Some of them were thermolyzed and decomposed thermally in air up to 500°C. No relationship between the decomposition temperature and the type of metal bonding could be observed; for example, the cobalt derivative (a salt) had a higher decomposition point than the copper compound (a complex). Pyrolysis resulted in pyridine, 2-aminopyridine, 2-cyanopyridine, and 2-amino-6-cyanopyridine. Moreover, there was no clear effect of the type of the metal ion on the course of the thermolysis of *AP*H metal

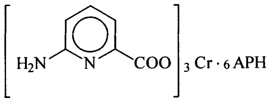
---

[*] Corresponding author

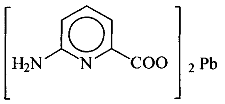
derivatives. It seemed therefore to be on interest to examine and compare the thermal properties of these compounds.



$(AP)_2\mathrm{Mn}$
1



$(AP)_3\mathrm{Cr}\cdot 6AP\mathrm{H}$
2



$(AP)_2\mathrm{Pb}$
3

In the present work, the thermal analysis (TG, DTA) of **1**–**3** in air and in helium atmosphere is presented. The salts have also been investigated by DSC (differential scanning calorimetry) in nitrogen atmosphere. The analysis of solid decomposition products was carried out using X-ray diffractograms.

Results and Discussion

TG and DTA analyses

The graphs of the thermal decomposition processes of compounds **1**–**3** in air and in helium atmosphere are shown in Figs. 1–3; the results are summarized in Tables 1 (air) and 2 (helium).

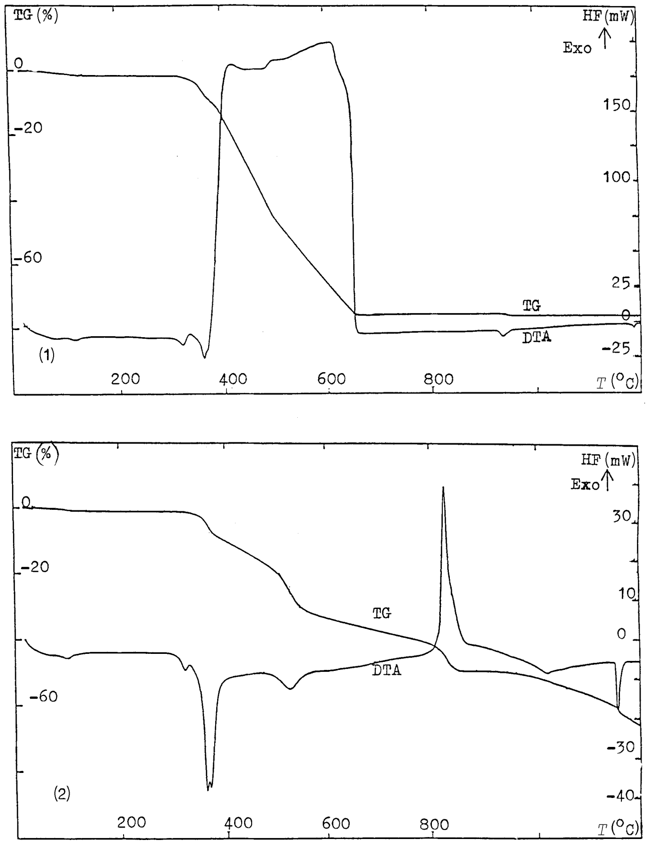


Fig. 1. TG and DTA curves for $(AP)_2\mathrm{Mn}$ recorded in air (1) and helium (2) atmosphere

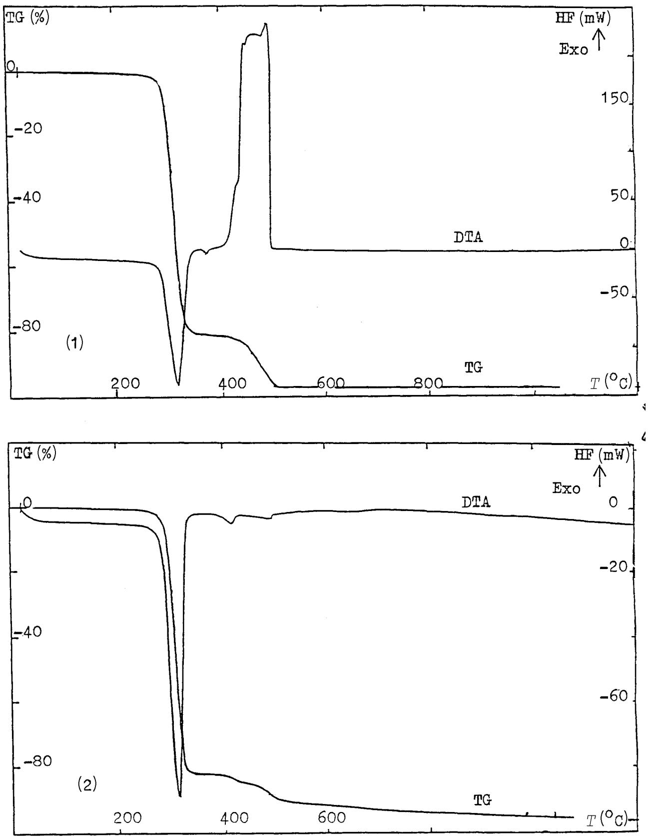


Fig. 2. TG and DTA curves for $(AP)_3Cr \cdot 6APH$ recorded in air (1) and helium (2) atmosphere

The analyses of the decomposition processes and of the solid products were performed using X-ray diffractograms [3], results of thermolysis [1], and literature data [4–10].

$(AP)_2Mn$

Compound **1** is thermally stable up to 200°C in air and to 290°C in helium; then thermal dissociation and decarboxylation take place. The mass losses are found to amount to 13.1% both in air and in helium (calcd.: 13.4%). In the second step (400–653°C), the TG curves in air show a very rapid and big mass loss corresponding to the liberation of 1.5 ligand molecules. The exothermic peak at 610°C originates from the oxidation process and the combustion of carbon remaining after the oxidation of organic fragments. Simultaneously, the manganese oxides are formed. X-ray diffraction patterns indicate the formation of Mn_3O_4 as a solid residue. The mass loss found is 62.4% (calcd.: 63.4%).

The decomposition process in helium atmosphere is more complex. The DTA curve indicates four steps. After the decarboxylation, the second mass loss corresponds to the release of 2-aminopyridine (found: 26.2%; calcd.: 28.5%). Elimination of $2\text{-}NH_2Py$ has also been observed during the thermolysis of other metal 6-aminopicolinates [1]. Further partial deamination takes place in the fourth

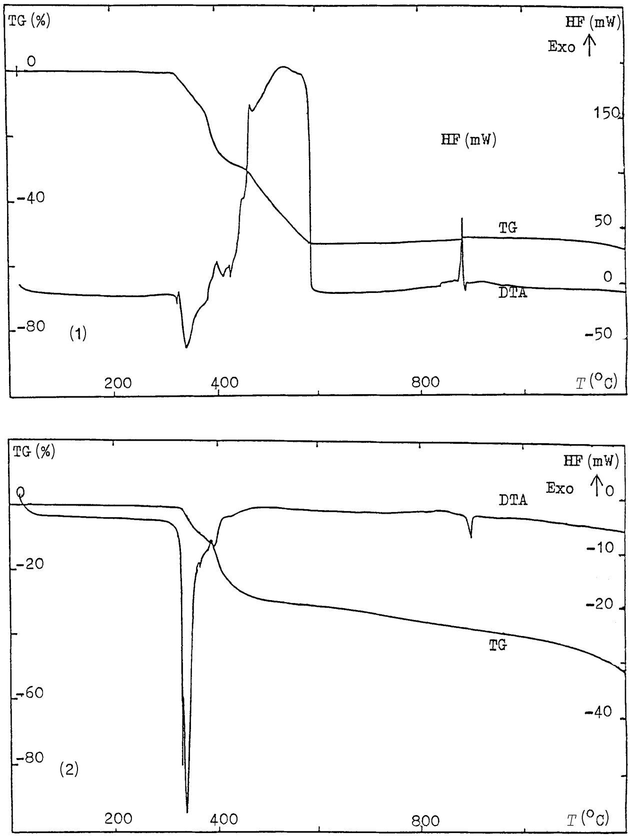


Fig. 3. TG and DTA curves for $(AP)_2Pb$ recorded in air (1) and helium (2) atmosphere

Table 1. Thermal decomposition characteristics in air

	Temp. range (°C)	Peak DTA temp (°C)	Mass loss (%) obs. (calcd.)	Process
$(AP)_2Mn$	200–400	359 endo	13.1 (13.4)	$-CO_2$
	400–653	610 exo	62.4 (63.4)	-1.5 *AP*; forms MnO_2 to Mn_3O_4
$(AP)_3Cr \cdot 6APH$	200–380	314 endo	81.2 (81.6)	-6 *AP*H, $-3CO_2$, -2-NH_2Py
	380–500	490 exo	15.3 (14.5)	deamination, forms Cr_2O_3
$(AP)_2Pb$	290–433	338 endo	28.1 (28.4)	$-CO_2$, -2-NH_2Py
	433–595	540 exo	25.0 (28.4)	-*AP*; forms PbO

step between 755 and 882°C. At the same time oxidation along with partial decomposition of the remaining fragments of the organic ligand occurs simultaneously with the oxidation of Mn to MnO and MnO_2. The mass loss found is 11.0% (calcd.: 10.4%). The conversion of MnO_2 into Mn_2O_3 and Mn_3O_4 proceeds slowly above 882°C. The X-ray patterns of the solid residue show that the major phase is Mn_2O_3 with minor amounts of MnO and Mn_3O_4.

Table 2. Thermal decomposition characteristics in helium

	Temp. range (°C)	Peak DTA temp. (°C)	Mass loss (%) obs. (calcd.)	Process
$(AP)_2$Mn	291–435	359, 370 endo	13.1 (13.4)	$-CO_2$
	435–755	525 endo	26.2 (28.5)	-2-NH_2Py
	755–882	831 exo	11.0 (10.4)	-0.25 *AP*; forms MnO, MnO_2; conversion to Mn_2O_3 and Mn_3O_4
$(AP)_3$Cr · 6*AP*H	200–372	310 endo	82.1 (81.6)	-6 *AP*H, $-3CO_2$, -2-NH_2Py
	372–1000	415, 481 endo	14.1 (14.5)	deamination, forms Cr_2O_3
$(AP)_2$Pb	315–373	344 endo	9.9 (9.1)	$-CO_2$
	373–564	397 exo	20.9 (19.5)	-2-NH_2Py
	564–1200	893 endo	20.7 (19.5)	-2-NH_2Py, forms PbO_2

(AP)$_3$Cr · 6*AP*H

A violent and rapid decomposition, accompanied by a sharp and strong endothermic peak and a big mass loss, is characteristic for the thermal curves obtained for **2** in air as well in helium atmosphere. The temperature range of the first decomposition steps and the corresponding mass losses are nearly identical in both environments (see Tables 1 and 2). The results of both processes are very similar. The compound begins to lose mass at 200°C; the sharp endothermic peak in the DTA curves is observed at 314 and 310°C in air and helium, respectively. The extremely big mass loss results from the release of 6 molecules of *AP*H (remaining after the hydrolysis of *AP*Na in the synthesis), the evolution of 2-aminopyridine (the main product of thermolysis), and decarboxylation. The found and the calculated mass losses associated with these processes are 81.1% (81.6%) and 82.2% (81.6%) in air and helium, respectively.

During further heating of the sample in air, the DTA curve exhibits an intense (nearly 250 mW) and broad exothermic peak at 490°C resulting from oxidation of organic fragments of the molecule. In this step, the deamination process-connected with the elimination of the remaining two molecules of 2-aminopyridine-occurs. Simultaneously, Cr_2O_3 is formed. According to the TG curve, the mass loss is 15.3% (calcd.: 14.5%). The second decomposition stage of **2** in helium atmosphere is similar to that in air. However, these processes are very slow, and no exothermic effect occurs. The observed mass loss (14.1%; calcd.: 14.5%) is due to a very slow deamination in the wide temperature range from 372 to above 1200°C. In air, mass stabilization is achieved earlier than in helium [10]. According to X-ray diffraction, the final solid decomposition product in both atmospheres is Cr_2O_3.

(AP)$_2$Pb

The DTA curve of **3** in air indicates two decompositions from 290 to 433°C and from 433 to 595°C. The first endothermic peak is sharp. The second exothermic peak is broad and can be considered as the result of reactions of different energetic effects taking place within the same temperature range. Initially, the organic anions dissociate with the elimination of 1 mol of CO_2. Deamination also takes place, and the formation of PbO_2 and PbO begins. The exothermic peak of the second decomposition step is connected with the oxidation of organic fragments, further partial deamination, and the formation of PbO [7]. Upon heating the sample to 1000°C, Pb_3O_4 is partially formed. This observation is confirmed by the exothermic effect at 879°C with the simultaneous small mass growth of 1.77%. In helium atmosphere, the first mass loss between 315 and 373°C corresponds to the decomposition of **3** and the endothermic decarboxylation process. Then, the DTA curve exibits an exothermic peak at 397°C, associated with the release and partial oxidation of the organic fragments and the formation of PbO_2. In the last deamination step, the remaining 2-NH_2Py is eliminated. It was impossible to achieve mass stabilization in helium, probably due to a slow reduction of PbO_2 to PbO.

DSC analyses

DSC analyses were performed in order to obtain quantitative results for the thermal effects accompanying the various processes ocurring during heating. The measurements were carried out at the same heatup rate as used for the TG-DTA investigation, but in a narrower temperature range according to operating range of a calorimeter. The DSC curves obtained for compounds **1**–**3** are presented in Fig. 4. A comparison of the TG curves and DSC analyses is a very useful tool in the investigation and characterization of the thermal behaviour of organic compounds [8]. The values of the thermodynamic quantities connected with the particular TG and DSC curves are presented in Table 3. The transition enthalpy values give information about the dimensions of thermal effects, being a sum of all processes taking place in the particular temperature range. The thermal parameters of the conversion of **1** and **3** are similar and are connected with the loss of the carboxyl group and the formation of CO_2 in both cases. The observed summarized thermal effect is not large and depends only little on the kind of metal in the molecule. In the case of compound **2**, the transition enthalpy is high. This effect is due to elimination of six molecules of *AP*H from the outer cooordination sphere, the release of three CO_2 molecules, and the elimination of 2-aminopyridine.

The present DSC research only approximately permits to think about the real value of thermal effect concomitant with proposed conversions. A thorough discussion of the processes involved in the thermal decomposition together with bond energy characterization and structure requires additional and more detailed DSC studies under different conditions.

The thermal properties of Mn(II) and Pb(II) picolinates are similar. The thermal decomposition characteristics are almost identical, especially in the lower temperature range (up to 500°C). The values of the transition enthalpy of the decarboxylation process are nearly identical and indicate a similar bond energy between the aromatic ring and the carboxylic group in Mn(II) and Pb(II) picolinates. The analogies in the thermal properties of these two compounds result most probably from their identical structure. According to a previous study [1],

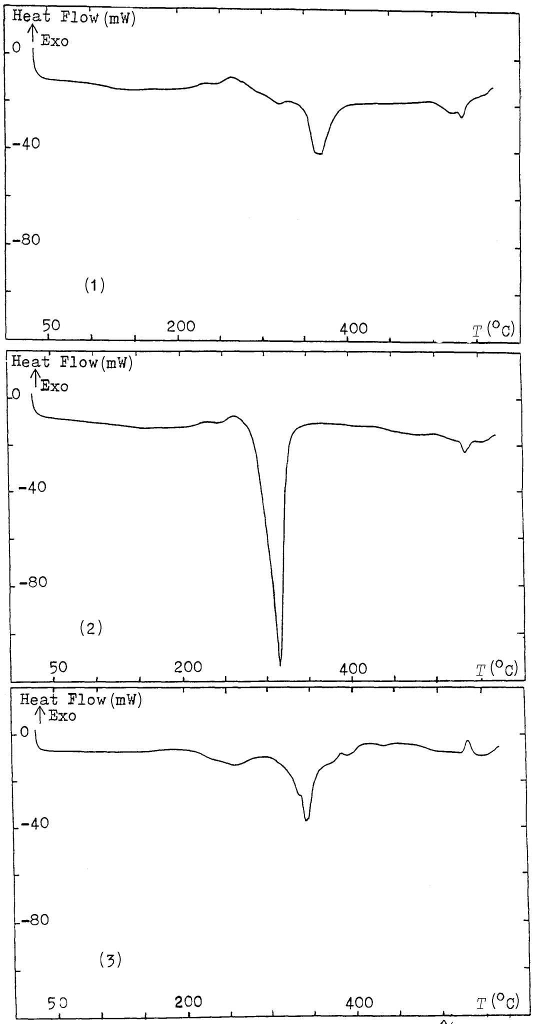


Fig. 4. DSC curves of $(AP)_2$Mn(1), $(AP)_3$Cr · 6*AP*H (2), and $(AP)_2$Pb (3)

Table 3. Thermodynamic parameters for thermal decomposition from TG and DSC curves

	TG		DSC		
	Temp. range (°C)	Δm (%)	Onset point T (°C)	Peak DSC endo T (°C)	*H* (J/mol)
$(AP)_2$Mn	291–435	13.1	351	368	85.2
$(AP)_3$Cr · 6*AP*H	200–372	82.1	295	315	1208.5
$(AP)_2$Pb	315–373	9.9	334	344	94.4

both compounds are organic salts. The difference in electronic configuration and size of Mn and Pb does not play any significant role in the process of the thermal dissociation of their *AP*H salts.

The behaviour of the chromium derivative during the thermal decomposition is different both with respect to the decomposition characteristic and the thermodynamic parameters. The reason for this difference is the bonding structure of **2** with an outer coordination sphere of six molecules of *AP*H. Thermal decomposition of $(AP)_3\mathrm{Cr} \cdot 6AP\mathrm{H}$ occurs in an almost identical manner in air and in helium atmosphere. A very intense and short exothermic process taking place in air at 420 – 500°C does not influence the pathway of thermal decomposition, but probably only accelerates the formation of stable Cr_2O_3. The stabilizing effect dominates over the oxidizing process, irrespective of the atmosphere.

Experimental

The thermal decomposition investigations were performed using a Setaram (Lyon, France) Thermal Analyser TG-DTA type 92–16 and a Differential Scanning Calorimeter (Setaram) DSC-92. During the measurements, the samples were heated in Pt or Al crucibles from room temperature to 1200°C (TG-DTA) and to 550°C (DSC) at a heating rate of 10 K/min. The mass changes and transformation energetics of the samples were measured. Data acquisition and evaluation as well as instrument control were carried out using a standard software package. The initial mass of the samples was in the range of 27–45 mg and 14–18 mg for TG-DTA and DSC measurements, respectively.

The results of the X-ray analyses, obtained on an X-ray diffractometer Siemens D500, were evaluated using the Powder Diffraction File [3].

References

[1] Baran W, Chaczatrian K, Tomasik P, Araki K (1995) Polish J Chem **69**: 1245
[2] Gill NS, Nuttal RM, Scaife DE, Sharp DWA (1961) J Inorg Nucl Chem **18**: 79
[3] Powder Diffraction File, International Center of Diffraction Data ICPDSICDD (1990) Park Lane, Swarthmore
[4] Wendlandt WW, Collins LW (1976) Thermal Analysis. Dowden, Hutchinson & Ross Inc, Stroudsburg, Pennsylvania
[5] Wendlandt WW, Smith JP (1967) The Thermal Properties of Transition Metal Amine Complexes. Elsevier, Amsterdam
[6] Czakis-Sulikowska D, Radwańska-Doczekalska J, Kuźnik B, Malinowska A (1995) Transition Met Chem **20**: 203
[7] Czakis-Sulikowska D, Radwańska-Doczekalska J, Kużnik B, Malinowska A (1996) Transition Met Chem **21**: 19
[8] Rodante F, Marrosu G, Catalani G (1992) Thermochimica Acta **194**: 197
[9] Rodante F (1992) Thermochimica Acta **200**: 47
[10] Czerwiński M, Kowalczyk B, Bragiel P (1994) Thermochimica Acta **231**: 151

Received July 7, 1997. Accepted (revised) October 6, 1997