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A STUDY OF SOLID-STATE THERMAL DECOMPOSITION CHARACTERISTICS OF SOME METALLO-ORGANIC COMPOUNDS

III. Dehydration and decarboxylation of hydrated calcium and some first row transition metal salts of pyridine-2-carboxylic acid

S. Ghosh, B. Sur, S. K. Ray* and *P. K. Ray*

DEPARTMENT OF INORGANIC CHEMISTRY, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA, 700 032, INDIA, * DEPARTMENT OF CHEMISTRY, CALCUTTA, 700 032, INDIA

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The solid-state dehydration of the hydrated Ca(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) salts of pyridine-2-carboxylic acid (picolinic acid) and subsequent decarboxylation of the corresponding anhydrous salts have been studied by simultaneous TG, DTA and DTG. The sequences of thermal stability of the hydrated and the anhydrous compounds have been established from analysis of the TG, DTA and DTG traces for dehydration of the hydrated salts and for decarboxylation of the anhydrous compounds. Thermal parameters such as activation energy, enthalpy change and order of reaction for the different stages of each process have been computed by standard methods. An attempt has been made to account for the observed trend in the thermal stability of the anhydrous salts towards decarboxylation. A mechanism of thermal decraboxylation of calcium picolinate has been proposed.

Experimental

Preparation of the compounds

The picolinic acid used was an L. R. BDH product. The Ca(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) salts of picolinic acid were prepared by reacting the respective metal carbonate (G. R. E. Merck) with the acid in hot aqueous solution. A slight excess of calcium carbonate was used in the preparation of hydrated calcium picolinate, followed by filtration and subsequent crystallization from the filtrate. In the preparation of the other metal picolinates, the acid was always kept in slight excess and the precipitated metal picolinates were washed with cold water and then dried over fused $CaCl_2$ for 48 hours.

Measurements and calculations

Simultaneous DTA, TG and DTG determinations of the salts were carried out with a Paulik–Paulik–Erdey type MOM derivatograph in dry air. The particle size of the

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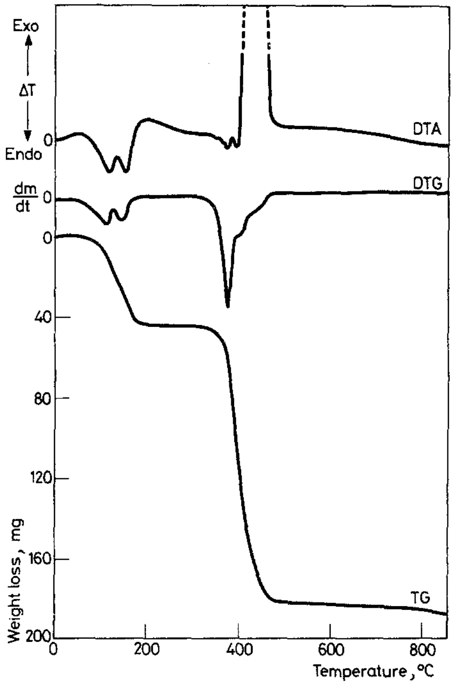

Fig. 1.1 Thermal curves of $Co(pic)_2 \cdot H_2O$

Table 1

Compound	% found (calcd.) M	 C	 H	 N
$Ca(pic)_2 \cdot H_2O$	13.30 (13.24)	23.78 (23.84)	1.35 (1.32)	4.71 (4.63)
$Mn(pic)_2$	18.20 (18.37)	24.15 (24.08)	1.30 (1.33)	4.75 (4.68)
$Co(pic)_2 \cdot 4\,H_2O$	15.55 (15.71)	19.31 (19.20)	1.05 (1.06)	3.80 (3.73)
$Ni(pic)_2 \cdot 4\,H_2O$	15.60 (15.66)	19.28 (19.21)	1.05 (1.06)	3.79 (3.73)
$Cu(pic)_2 \cdot 0.5\,H_2O$	20.15 (20.07)	22.80 (22.74)	1.27 (1.26)	4.50 (4.42)
$Zn(pic)_2 \cdot 4\,H_2O$	17.25 (17.14)	18.93 (18.87)	1.03 (1;04)	3.72 (3.67)

samples was in the range 100–150 mesh. The heating rate was about 4.25 deg/minute, and a sample size of 210–230 mg was used to make the volume nearly the same in each case. The reference material was aluminium oxide previously heated to 1600°. The sample holder and the reference holder were made of platinum. The metals were analyzed by standard procedures: carbon, hydrogen and nitrogen were determined by microanalytical techniques. The hydrated and anhydrous compounds were characterized by recording their ir spectra in a halocarbon mull on a Beckman IR 20A spectrophotometer. Procedures adopted for evaluation of the different kinetic parameters, such as the activation energy and the enthalpy change accompanying the dehydration and decarboxylation processes, have been described elsewhere [1]. The results of the elemental analyses are given in Table 1.

Results and discussion

Dehydration process

On gradual heating from room temperature, the hydrated salts were completely dehydrated within the temperature range 70–240°. From the TG, DTG and DTA traces of the dehydration stage, it was found that calcium picolinate monohydrate, copper(II) picolinate semihydrate and zinc picolinate tetrahydrate lost their crystallization water in a single step, while cobalt(II) and nickel(II) picolinate hydrates lost their water in two steps. For hydrated calcium, copper(II) and zinc picolinates, the one-step dehydration process may be represented as:

$$M^{II}(C_6H_4NO_2)_2 \cdot x\,H_2O = M(C_6H_4NO_2)_2 + x\,H_2O \quad (1)$$

where $M^{II} = Ca$, $x = 1$; $M^{II} = Cu$, $x = 0.5$; $M^{II} = Zn$, $x = 4$. For the two-step dehydration of hydrated cobalt(II) and nickel(II) picolinates, the general reactions are

$$M^{II}(C_6H_4NO_2)_2 \cdot x\,H_2O = M^{II}(C_6H_4NO_2)_2 \cdot y\,H_2O + z\,H_2O \quad (2a)$$

$$M^{II}(C_6H_4NO_2)_2 \cdot y\,H_2O = M^{II}(C_6H_4NO_2)_2 + y\,H_2O \quad (2b)$$

where $M^{II} = Co, x = 4, y = 1.5, z = 2.5$; $M^{II} = Ni, x = 4, y = 2, z = 2$. The initiation, peak and completion temperatures of the dehydration of each species, as obtained from the relevant DTG traces, are given in Table 2, together with the corresponding weight losses. The enthalpy change accompanying the dehydration of each species was determined by a standard method [2]. The order of reaction was also determined by standard methods [3, 4]. The activation energy for each dehydration process was computed from analysis of the corresponding TG traces, using the method of Horowitz and Metzger [3]. The results obtained are tabuleted in Table 2. The ir spectra of the hydrated and the anhydrous varieties were recorded and compared to ascertain the completion of the dehydration process.

Table 2

Reaction	Initiation temp., °C	Peak temp., °C	Completion temp., °C	Loss in wt.%		E_{Act}, kJ/mole	ΔH, kJ/mole	Order of reaction
				Calc.	Found			
$Ca(pic)_2 \cdot H_2O \rightarrow Ca(pic)_2 + H_2O$	160	199	240	5.96	5.88	217.9	109.7	1
$Co(pic)_2 \cdot 4\,H_2O \rightarrow Co(pic)_2 \cdot 1.5\,H_2O + 2.5\,H_2O$	70	130	140	12.00	11.30	95.6	71.9	1
$Co(pic)_2 \cdot 1.5\,H_2O \rightarrow Co(pic)_2 + 1.5\,H_2O$	140	160	187	8.18	9.06	196.8	63.9	1
$Ni(pic)_2 \cdot 4\,H_2O \rightarrow Ni(pic)_2 \cdot 2\,H_2O + 2\,H_2O$	70	128	140	9.60	10.00	114.8	105.2	1
$Ni(pic)_2 \cdot 2\,H_2O \rightarrow Ni(pic)_2 + 2\,H_2O$	155	194	219	10.62	10.98	146.7	106.2	1
$Cu(pic)_2 \cdot 0.5\,H_2O \rightarrow Cu(pic)_2 + 0.5\,H_2O$	70	81	96	2.84	2.60	—*	24.2	1
$Zn(pic)_2 \cdot 4\,H_2O \rightarrow Zn(pic)_2 + 4\,H_2O$	70	122	160	18.87	18.69	114.3	256.0	1

* Activation energy could not be determined by Horowitz and Metzger's method as the TG trace was very steep.

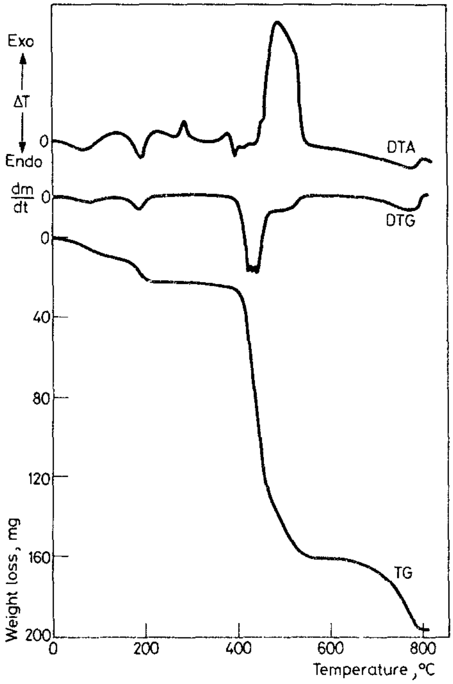

Fig. 1.2 Thermal curves of $Ca(pic)_2 \cdot H_2O$

Decarboxylation process

All the anhydrous picolinates exhibit considerable thermal stability; they undergo decarboxylation within the temperature range 288–540°. The TG traces exhibit a two-stage decarboxylation process, with the first break in each TG curve corresponding to an unusual composition. Unfortunately, we could not isolate and characterize these unstable intermediates of unusual composition. The first break is followed by the second and final break, leading to the oxide end-product. This observation is corroborated by the corresponding DTA and DTG traces, which exhibit two distinctly separate stages in each case. The DTA traces show an early small endotherm, followed by a large exotherm. The small endotherm may be due to the absorption of heat during the first stage of the decarboxylation process, leading to formation of the unstable intermediate, while the large exotherm may be attributed to the net heat change involved in the second stage of decarboxylation, comprising the heat evolved due to the decomposition of the intermediate into metal oxide and gaseous products, and the heat evolved due to secondary reactions between the different gaseous products. The fact that both stages of thermal decomposition after dehydration are manifestations of the decarboxylation process is indicated by the evolution of carbon dioxide through the entire course of this reaction. The initiation, peak and completion temperatures for the two-stage decarboxylation of the anhydrous picolinates are

Table 3

Compound undergoing decarboxylation	Stages of decarboxylation	Initiation temp., °C	Peak temp., °C	Completion temp., °C	Loss in wt.% Calc.	Loss in wt.% Found	E_{Act}, kJ/mole	ΔH, kJ/mole	Order of reaction
Ca(pic)$_2$	Stage — I	380	445	468	—	49.51	137.3	85.1	1
	Stage — II	468	—*	540	30.23	31.70	221.3	535.2	1
Mn(pic)$_2$	Stage — I	352	437	451	—	65.84	375.0	19.6	1
	Stage — II	451	—*	518	30.56	30.43	216.2	900.1	1
Co(pic)$_2$	Stage — I	329	393	416	—	60.65	218.3	167.9	1
	Stage — II	416	—*	484	37.50	36.80	319.5	808.1	1
Ni(pic)$_2$	Stage — I	330	388	414	—	62.71	219.2	84.9	1
	Stage — II	414	—*	478	33.80	37.20	318.2	594.4	1
Cu(pic)$_2$	Stage — I	292	309	323	—	58.29	—+	42.6	1
	Stage — II	323	—*	448	38.00	35.48	101.4	1082.8	1
Zn(pic)$_2$	Stage — I	288	393	401	—	62.36	222.8	58.7	1
	Stage — II	401	—*	497	30.97	31.42	185.1	440.2	1

+ Activation energy could not be determined by Horowitz and Metzger's method as the TG trace was very steep.

* No peak but a plateau in the DTG trace could be found.

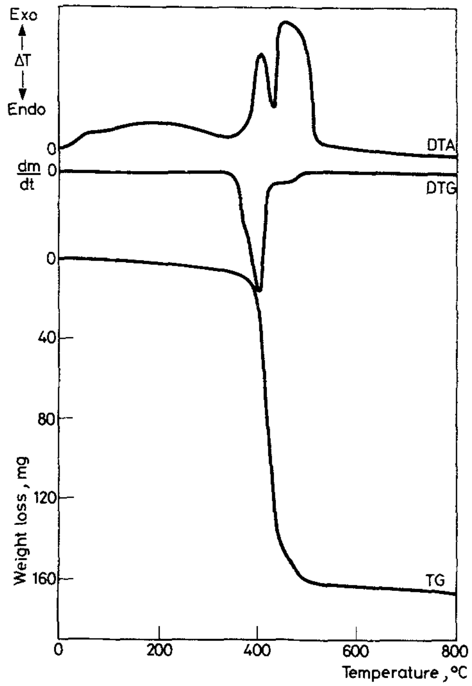

Fig. 1.3 Thermal curves of $Mn(pic)_2$

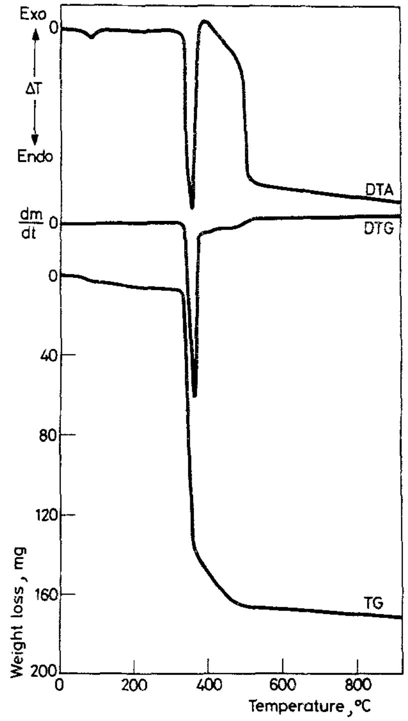

Fig. 1.4 Thermal curves of $Cu(pic)_2 \cdot 0.5\ H_2O$

given in Table 3, together with the corresponding weight losses. The final products remaining in the crucible were found to be mainly the oxides of the metals; they were identified by chemical analysis and through their X-ray diffraction patterns. The order of reaction for the decarboxylation process was found to be unity in all cases. With the same methods as used in the dehydration process, the activation energies of the decarboxylation process in both stages were evaluated from the $\ln \ln \frac{W_0 - W_t^f}{W - W_t^f}$ vs. θ plots. The enthalpy change accompanying each decarboxylation process was measured from the DTA traces, and are presented in Table 3.

The plots of initiation (t_i), peak (t_p) and completion temperatures (t_c) of thermal decomposition of the anhydrous metal picolinates against the negative heat of formation ($-\Delta H_f^0$) of the corresponding metal oxides [5] exhibit some interesting trends. as the solid end-product remaining in the crucible was the metal oxide in all cases, and as the negative heat of formation ($-\Delta H_f^0$) of the metal oxide is a relative measure of the strength of the M—O bond in the metal picolinate, the thermal stabilities of these compounds should gradually decrease in the sequence Mn(II) salt > Zn(II) salt >

Ni(II) salt > Co(II) salt > Cu(II) salt. Our observations closely follow this expected general sequence, with the exception of the zinc salt, which exhibited a minimum value. Plots of the peak and completion temperatures against $-\Delta H_f^0$ for the metal oxides exhibited nearly similar trends, the nickel and zinc salts showing some deviation from the expected general sequence.

Table 4

Compounds	Initiation temp., °C	Peak temp., °C	Completion temp., °C	ΔH_f^0 of oxides [13] kJ/mole
$Mn(pic)_2$	352	437	451	−384.6
$Co(pic)_2$	329	393	416	−239.0
$Ni(pic)_2$	330	388	414	−244.1
$Cu(pic)_2$	292	309	323	−155.1
$Zn(pic)_2$	288	390	401	−347.7

Table 5

Compounds	Initiation temp., °C	$i/r\ A^{0-1}$ [14]
$Ca(pic)_2$	380	1.000
$Mn(pic)_2$	352	1.219
$Co(pic)_2$	329	1.351
$Ni(pic)_2$	330	1.428
$Cu(pic)_2$	292	1.369
$Zn(pic)_2$	288	1.333

Plots of the initiation temperature (t_i) of the thermal decarboxylation of the metal picolinates against the reciprocal ionic radii [6] exhibited some definite trends. with gradual increase in the $1/r$ value for the corresponding metal ions.

A single break in the TG traces of Ca(II), Cu(II) and Zn(II) picolinate hydrates, and a single endotherm in each of the corresponding DTA and DTG traces, definitely indicates that all the water molecules are released simultaneously and hence are similarly bound. As is evident from the two endotherms in the corresponding DTA and DTG traces, the two-step dehydration of the cobalt and nickel picolinate tetrahydrates is indicative of the fact that the water molecules are bound differently. For cobalt picolinate tetrahydrate, 2.5 molecules of water are lost in the first stage of dehydration, and 1.5 molecules in the second stage. For nickel picolinate tetrahydrate, 2 molecules of water are lost in the first stage, and 2 molecules in the second stage. In the single-step dehydration and in the first step of the two-step dehydration processes, represented by the general equation in Table 1, the activation energies follow the sequence Ca > Ni > Zn > Co. The overall enthalpy changes for the dehydration processes, however, follow the sequence Ca > Zn > Ni > Cu > Co. The thermal stabilities of the metal picolinate hydrates, obtained from the DTG peak temperature, follow the sequence Ca > Co > Ni > Zn > Cu.

In the first stage of the decarboxylation of the anhydrous metal picolinates, represented by the equation in Table 2, the activation energies follow the sequence Mn > Zn > Ni > Co > Ca. The overall enthalpy changes for the decarboxylation processes, however, follow the sequence Cu > Co > Mn > Ni > Ca > Zn. The thermal stabilities of the anhydrous metal picolinates, from the DTG initiation and peak temperatures, follow the sequence Ca > Mn > Zn ~ Co > Ni > Cu.

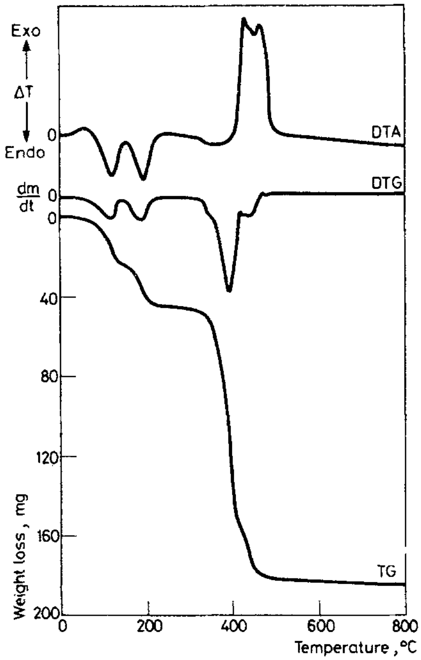

Fig. 1.5 Thermal curves of $Ni(pic)_2 \cdot 4\,H_2O$

The general series found by Irving and Williams [7] for the stability of complexes in solution is the reverse of the thermal stability sequence found for the metal picolinates in the solid state in this study. The same sequence was reported earlier for the thermal stabilities of other compounds of the same metal ions [8–12]. This behaviour may be accounted for by assuming that the strengths of the intermolecular bonds play a significant role in determining the thermal stabilities of the solid compounds, and the thermal stability varies in the proposed sequence due to the nature of the variation of the intermolecular bond strengths in the crystal lattices of the metal picolinates.

Some of the products of decomposition were characterized with a glass apparatus resembling one used in the purification of organic compounds by sublimation.
The lower portion of the apparatus was placed inside a small furnace, which was heated to the desired temperature range. The sample (~ 100 mesh) was placed at the bottom of the wide outer tube, while the other tube of the apparatus was connected to bubblers filled with the required reagents for the absorption and subsequent identification of the gaseous products of decomposition. On heating to the required temperature range, a white sublimate was collected on the outer face of the inner tube, through which cold water was circulated. After the heating was over and the apparatus was allowed to cool to room temperature, the white deposits were scraped off. They were subjected to elemental analysis and physical (m. p., ir spectra) and chemical tests (such as the formation of the red [Fe(dipy)$^{+2}$] complex and its identification via its electronic spectrum) and were identified as the various bipyridines. Among the gaseous products, pyridine, carbon dioxide and carbon monoxide were detected, and the residue remaining in the wide tube was found to be the oxide of the metal. In the case of calcium picolinate the residue was calcium carbonate.

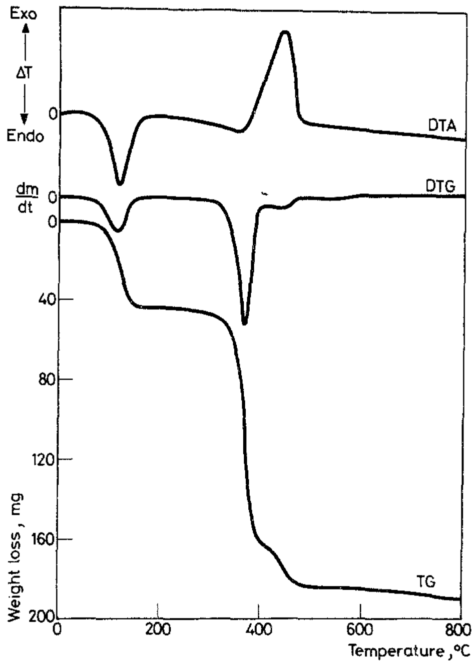

Fig. 1.6 Thermal curves of $Zn(pic)_2 \cdot 4 H_2O$

The whole experiment was then repeated after displacement of the air inside the apparatus by pure dry nitrogen, which was passed slowly during the entire course of decomposition. The same products were detected in this case.

Under these circumstances, it appears that the decarboxylation reaction proceeds through a free-radical mechanism; this is corroborated by the formation of the bipyridines, by the coupling of two pyridyl free radicals and also by the formation of pyridine through the abstraction of a hydrogen by one pyridyl radical from another.

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Zusammenfassung — Die Dehydratisierung der hydratisierten Ca(II)-, Mn(II)-, Co(II)-, Ni(II)-, Cu(II)- und Zn(II)-Salze der Pyridin-2-carboxylsäure (Picolinsäure) in fester Phase und die nachfolgende Decarboxylierung der entsprechenden wasserfreien Salze wurden mittels simultaner TG, DTA und DTG untersucht. Aus den thermoanalytischen Kurven wurde die der thermischen Stabilität entsprechende Reihenfolge der hydratisierten und wasserfreien Verbindungen ermittelt. Thermische Parameter wie Aktivierungsenergie, Enthalpieänderung und Reaktionsordnung wurden für die einzelnen Schritte jedes Prozesses nach Standardmethoden berechnet. Es wurde ein Versuch unternommen, den Trend in der thermischen Stabilität der wasserfreien Salze gegenüber Decarboxylierung zu erklären. Ein Mechanismus der thermischen Decarboxylierung von Calciumpicolinat wird vorgeschlagen.

Резюме — Совмещенными методами ТГ, ДТА и ДТГ изучена твердотельная дегидратация кристаллогидратов пиколинатов двухвалентных кальция, марганца, кобальта, никеля, меди и цинка, а также последующее декарбоксилирование соответствующих безводных солей. Установлена последовательность термоустойчивости гидратов и безводных солей. Для различных стадий каждого процесса рассчитаны энергия активации, изменение энтальпии и порядок реакции. Сделана попытка рассмотреть корреляцию между термической устойчивостью безводных солей и их декарбоксилированием. Для кальциевой соли пиколиновой кислоты предложен механизм термического декарбоксилирования.