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COMPLEXES OF DIVALENT METAL IONS WITH CINCHOMERONIC AND DINICOTINIC ACID

THERMAL PROPERTIES

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ABSTRACT

The thermal properties of the complexes of cinchomeronic and dinicotinic acid with several divalent metal ions were determined by thermogravimetry (TG) and differential thermal analysis (DTA).

For the thermal stability of the anhydrous compounds a sequence may be observed for the metal ions with cinchomeronic (3,4-H_2PC) and dinicotinic acid (3,5-H_2PC):

$$Mn > Fe > Co > Ni > Cu < Zn$$

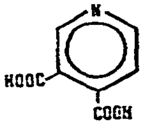
The thermal stability of the pyridine carboxylic acid for each metal of the series is:

dinicotinic > cinchomeronic

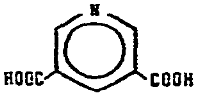
The activation energy values for each thermal reaction were also calculated, using the Coats and Redfern algorism, by the Univac 1108 computer, by a program properly implemented for the statistical analysis of the data to obtain the reaction order and the activation parameters with the relative confidence limits.

INTRODUCTION

In the series of our research on the behaviour of compounds obtained by the reaction between metal ions and heterocyclic ligands[1–8] the complexes of cinchomeronic acid (pyridine-3,4-dicarboxylic acid) 3,4-H_2PC and



3,4-H_2PC



3,5-H_2PC

of dipicolinic acid (pyridine-3,5-dicarboxylic acid) 3,5-H_2PC with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) were examined by thermal analysis.

EXPERIMENTAL

Instrumentation

Du Pont 951 thermobalance. Du Pont 990 thermal differential analyser. Radiometer PHM 22r potentiometer.

A heating rate of 10°C min^{-1} was employed. Atmosphere: air or nitrogen.

Preparation of compounds

Cinchomeronic acid and dinicotinic acid (Aldrich Chemical Co., Inc., Milwaukee, Wisc.) were used. Other chemicals employed were of reagent grade.

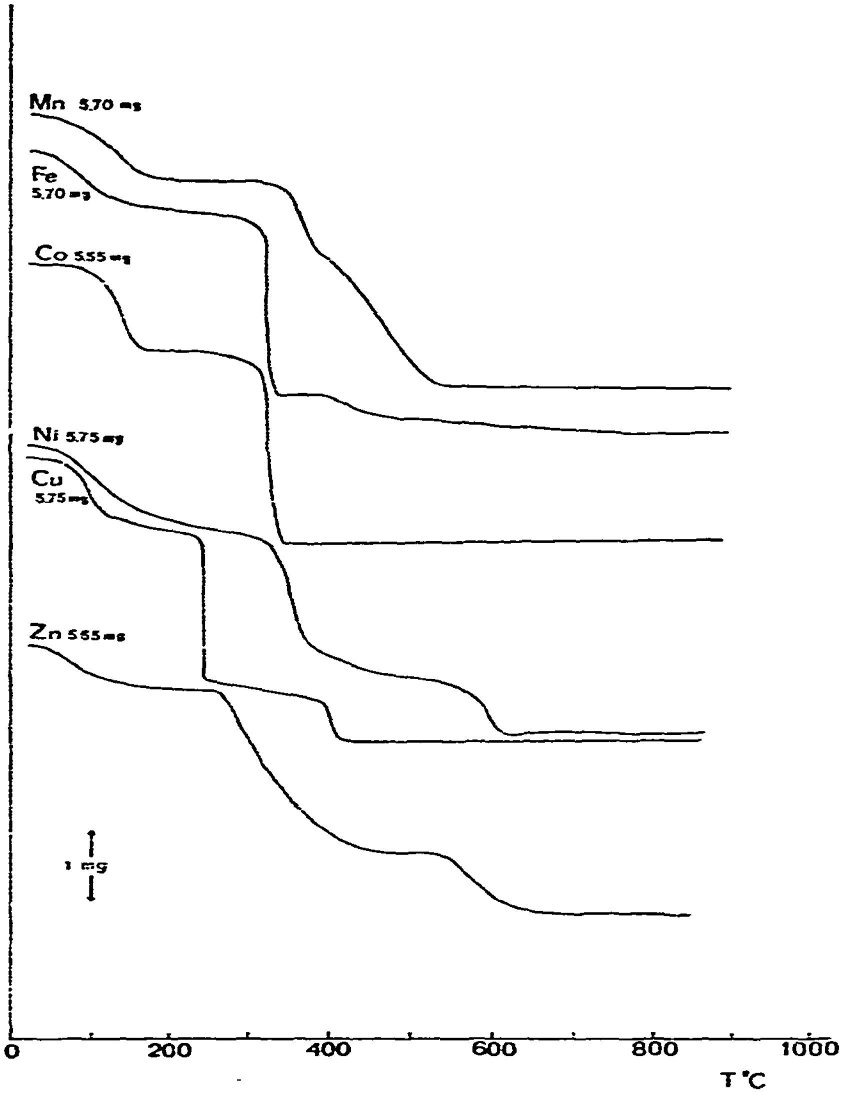


Fig. 1. TG curves of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) pyridine-3,4-dicarboxylates. Heating rate, 10°C min^{-1}; air atmosphere.

The compounds were prepared in the same way as the complexes of quinolinic acid[6].

All the precipitates were dried in vacuo for 48 h at room temperature. Thermogravimetry was used to determine the water content and the residual metal oxide; the metal content was also established by compleximetric titration of the anhydrous compound.

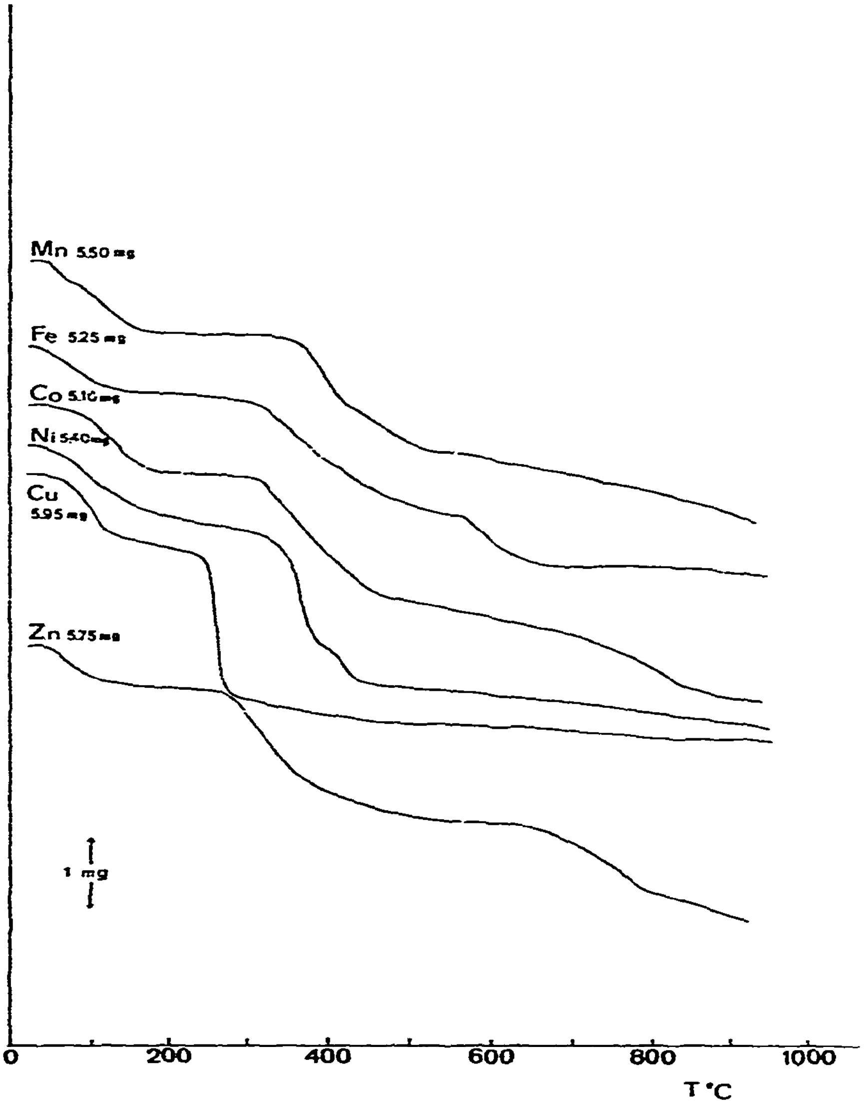


Fig. 2. TG curves of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) pyridine-3,4 dicarboxylates. Heating rate, 10 °C min^{-1}; N_2 atmosphere.

RESULTS

The TG curves in air and in nitrogen for all the 3,4-H_2PC complexes are given in Figs. 1 and 2. Only in the case of the cobalt complex in air the decomposition appeared to be a single-step process giving the metal oxide directly, while for all the other metal complexes the decomposition appeared to be a two-step process giving the oxide as final compound in air atmosphere. The first decomposition step gives carbonates or mixtures of oxides and carbonates.

DTA curves are given in Fig. 3; in a nitrogen atmosphere only endothermic peaks were found.

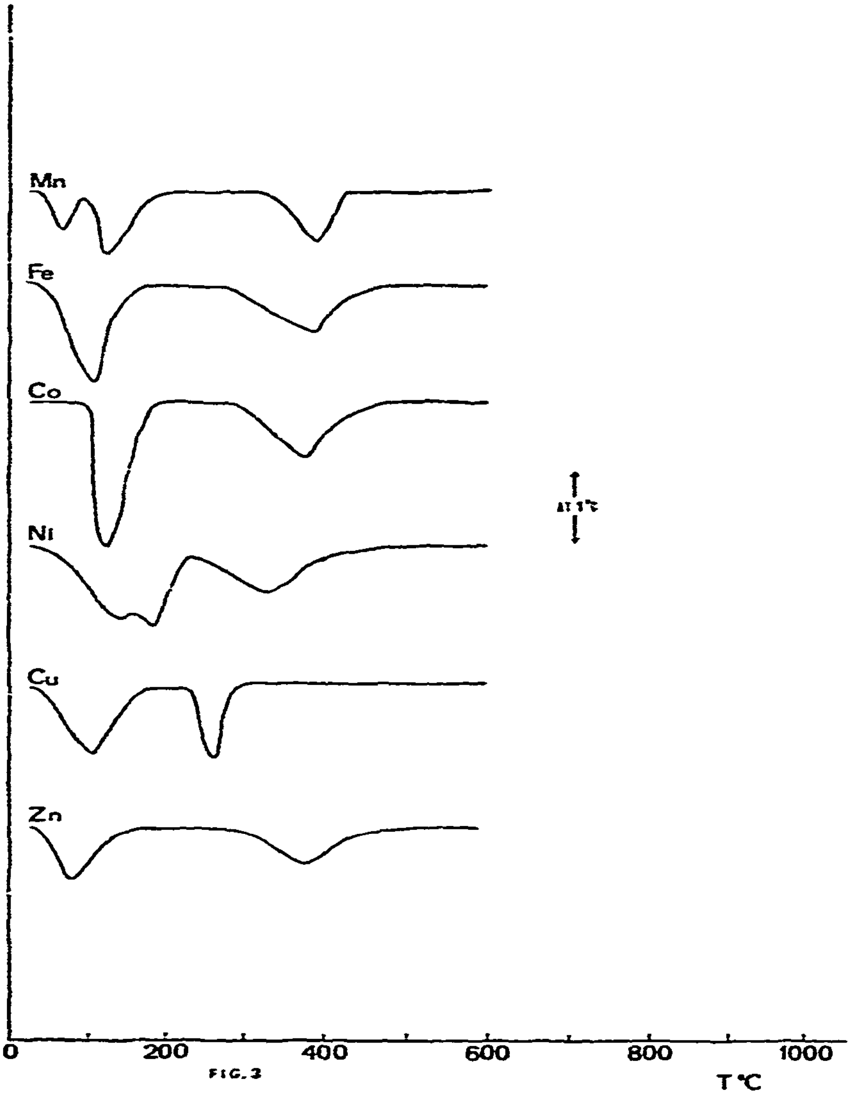


Fig. 3. DTA curves of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) pyridine-3,4 dicarboxylates. Heating rate, 10 °C min^{-1}; N_2 atmosphere.

The TG curves in air and in nitrogen for all the 3,5-H_2PC complexes are given in Figs. 4 and 5. The decomposition in air appeared to be a single-step process for manganese, iron, cobalt, nickel and zinc giving the metal oxide directly while for the copper complex the decomposition takes place in two steps, giving the carbonate and the oxide, respectively. The decomposition in nitrogen is always a two-step process. Figure 6 shows the DTA curves in nitrogen; only endothermic peaks were found.

The different behaviour of the 3,4-H_2PC and 3,5-H_2PC complexes can be justified considering the pdt's of the anhydrous compounds with regard to the pdt's of the corresponding carbonates.

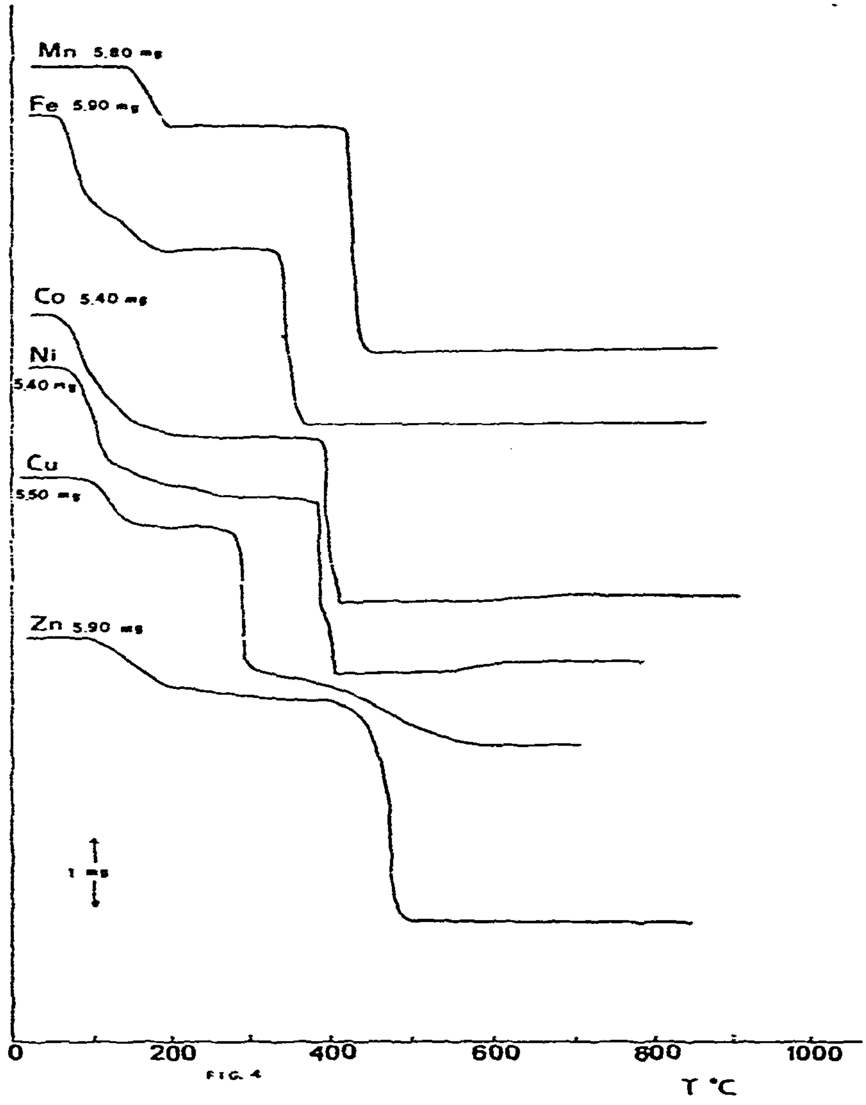


Fig. 4. TG curves of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) pyridine-3,5 dicarboxylates. Heating rate, 10°C min^{-1}; air atmosphere.

The TG curves were also used to calculate the activation energy. To minimize the errors and to standardize the process, the TG curves were obtained by using a platinum cylindrical sample holder 10 mm diameter, 3 mm depth with a 1 mm sample layer. The sample particle sizes ranged between 100 and 120 mesh. The purge gas was very pure (99,99%) nitrogen at 20 l h^{-1}.

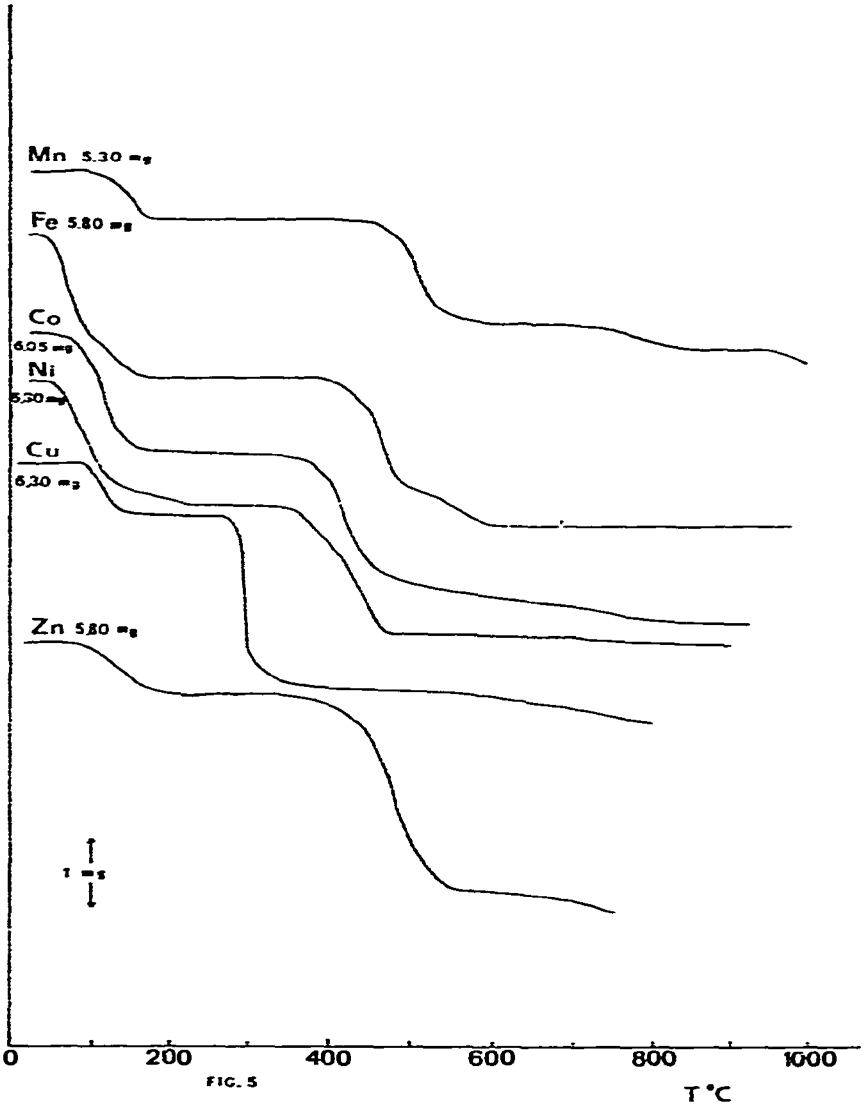


Fig. 5. TG curves of manganese(II), iron(II), cobalt(II), nickel(II) copper(II) and zinc(II) pyridine-3,5 dicarboxylates. Heating rate, 10°C min^{-1}; N_2 atmosphere.

METHOD OF CALCULATIONS

The integral expression obtained from Coats and Redfern[9] was used in the present work to obtain kinetic parameters. This approach was preferred to the differential one pointed out by Thomas et al.[10] owing to the fact that the number of data required to sample an experimental curve is lower than that needed to perform a derivation process.

To obtain a great number of data with the required accuracy a digital support (punched tape for example) or directly a computer would be useful as output of the

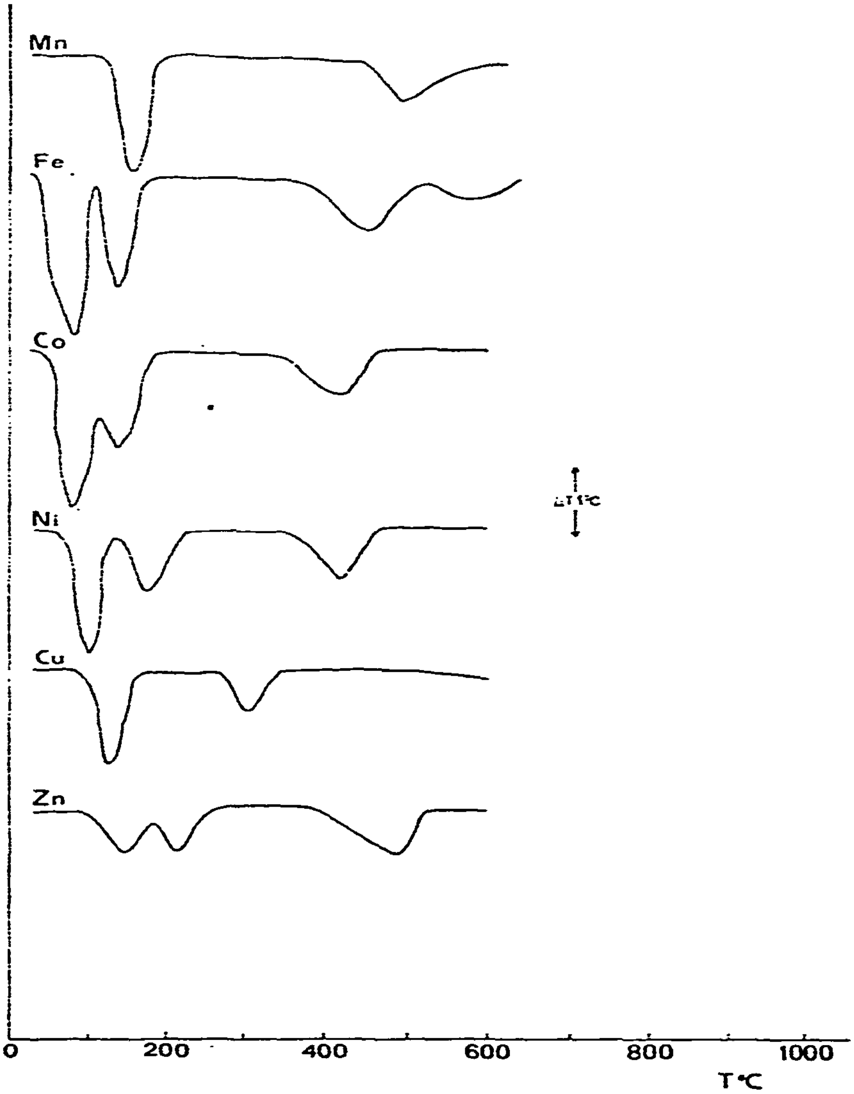


Fig. 6. DTA curves of manganese(II), iron(II), cobalt(II), nickel(II) copper(II) and zinc(II) pyridine-3,5 dicarboxylates. Heating rate, 10°C min^{-1}; N_2 atmosphere.

TG apparatus. Contrarily, in this work, data were manually sampled from recorded curves, punched on cards and analyzed by a Univac 1108 computer.

The above cited integral method is based upon the ability to distinguish a straight line between a curve family. This check was automatically done by means of the Snedocor test applied to the point distribution.

A, E and n were determined for the equation

$$\frac{d\alpha}{dt} = Ae^{-E/RT}(1-\alpha)^n$$

where α is the reaction degree, and the relation $a = dT/dt$ is assumed for the heating rate, with contant a.

Flow description of the program used, written in FORTRAN V

1. Read in data cards:
   - — Reaction orders to be checked ORD(I), I = 1,5
   - — Total weight change for the examined step WTOT
   - — Weight at the end of examined step W0
   - — Heating rate RATE
   - — Number of weight–temperature couples N
   - — Weight temperature couples Y(I), X(I), I = 1,N
2. Calculation of the reaction degree and of the reciprocal absolute temperature

$$\left.\begin{array}{l} \mathrm{Y1(I) = (Y(I)-W0)/WTOT} \\ \mathrm{X1(I) = 1./(X(I)+273.1)} \end{array}\right\} \mathrm{I = 1,N}$$

3. Minimization by the least squares method of the integral Coats expression parameters and calculation of ln A, E, $\sigma_{\ln A}$ and σ_E. Values of A are logarithmic because they may exceed single precision.
4. Calculation of Snedocor parameter F, residual variance S, correlation coefficient RHO.
5. Output of ln A, $\sigma_{\ln A}$, E, σ_E, S, ROH, F.
6. Repeat steps 3 to 5 for each assigned reaction order ORD(I).
7. Output on line printer of a graphic plot of regression lines and experimental points for the various orders of reaction with different symbols.
8. End of program.

In this way it is possible to select the order of the reaction for which the better straight line is obtained: F is maximum in correspondence to this value. Plots allow to have the same response also by graphic evaluation.

The program may be repeated in a trial-and-error process to give the best reaction order around the one obtained. However, in our opinion, an accuracy in the reaction order better than 0.5 would be meaningless with a set of 7 to 18 data points.

Confidence intervals reported in Table 1 for the E values were obtained in the usual manner multiplying standard errors by the t (Student parameter) values for the appropriate degrees of freedom at a confidence level of 0.95.

TABLE 1

T_1 = start of process temperature (°C); $\overline{T}$ = maximum rate process temperature (°C); T_2 = end of process temperature (°C); E^* = activation energy (kcal mol^{-1}); ORD = reaction order; DOF = degrees of freedom.

Me (3,4-PC)									*Me (3,5-PC)*							
Metal	*H_2O*	*React.*	*T_1*	*$\overline{T}$*	*T_2*	*E^**	*ORD*	*DOF*	*H_2O*	*React*	*T_1*	*$\overline{T}$*	*T_2*	*E^**	*ORD*	*DOF*
Mn	2	$-0.3H_2O$	30	65	85	15.3±0.7	1	6	2	$-2H_2O$	120	160	185	22.4±1.7	1	4
	1.7	$-1.7H_2O$	85	125	175	17.5±0.2	2	6	—	dec	445	500	650	53.4±2.5	2	9
	—	dec	350	390	490	63.1±5.7	>3	9								
Fe	2	$-2H_2O$	30	110	175	14.9±0.5	3	8	6	$-4H_2O$	40	90	110	28.6±2.3	2	8
	—	dec	275	385	500	12.5±1.0	1	16	2	$-2H_2O$	110	135	175	28.6±1.7	2	7
									—	dec	375	460	500	50.8±2.7	1	6
Co	4	$-4H_2O$	80	135	175	10.4±0.2	1	7	6	$-6H_2O$	60	110	185	20.1±1.7	2	6
	—	dec	290	380	510	24.4±1.5	2	14	—	dec	350	425	505	60.3±3.7	2	6
Ni	3.5	$-3.5H_2O$	30	150	270	14.7±0.4	4	12	6	$-5.3H_2O$	50	95	125	15.0±1.3	1	5
	—	dec	270	365	490	55.4±5.2	3	9	0.7	$-0.7H_2O$	125	180	225	10.4±1.5	2	6
									—	dec	350	425	470	29.3±3.7	1	8
Cu	3	$-3H_2O$	30	100	190	15.6±1.2	2	6	2	$-2H_2O$	75	125	155	23.5±10.1	2	9
	—	dec	230	260	305	130.0±31.0	>5	6	—	dec	270	300	345	118.0± 5.0	2	6
Zn	1.5	$-1.5H_2O$	30	95	160	23.5±0.4	4	11	2	$-2H_2O$	110	150	180	20.7±1.2	>3	6
	—	dec	265	360	480	40.4±0.4	>5	14	—	dec	420	470	520	31.4±0.7	2	9

DISCUSSION

When considering the thermal stability of the hydrated compounds no particular conclusions may be drawn: water is lost in a wide temperature range for all compounds as found elsewhere[5].

For the thermal stability of the anhydrous compounds the following sequence may be observed for the metal ions: Mn>Fe>Co>Ni>Cu<Zn in both series of compounds with 3,4-PC and 3,5-PC.

The thermal stability of the pyridine carboxylic acid for each metal of the series is: 3,5-PC>3,4-PC.

Thermal stability order is the reverse of the Lewis acidity of metal ion reported by Irving and Williams[11].

An explanation for this behaviour has been given previously[5].

However, to confirm the above assumptions, it is interesting to note that the thermal stability order is also the reverse of the ion "electronegativity density".

This latter value may be estimated from the second and third ionization potentials, I_2 and I_3 respectively, and from ionic radii R as

$$(I_2+I_3)/R^2$$

For the examined series:

Metal	I_2 *(kcal mol^{-1})*[a]	I_3 *(kcal mol^{-1})*[a]	R^b *(Å)*[a]	$(I_2+I_3)/R^2$
Mn	361	784	0.80	14.9
Fe	373	692	0.76	15.1
Co	393	785	0.78	16.1
Ni	418	830	0.78	17.1
Cu	468	875	0.69	23.5
Zn	414	922	0.74	20.3

[a] From G. H. Aylward and T. J. V. Findlay, *Chemical Data Book*, J. Wiley, Australasia, Pty. Ltd. (1966).

When considering the two series of compounds obtained with 3,4-H_2PC and 3,5-H_2PC, the thermal stability order agrees with a model similar to that proposed to explain the sequence of the metal ions series[5].

In fact when in the 3,5-pyridinedicarboxylic acid functional groups, e.g., carboxylates and aza's, are considered, they cannot be conjugated while in the 3,4-pyridinedicarboxylic acid they can. Moreover, in this latter case also a chelation may occur causing an increase in the intramolecular bonds and thus a decrease in the intermolecular ones, with a consequent decrease in the thermal stability.

A series of pyridinecarboxylic acids compounds with a polarizable metal ion as cadmium(II) has also been examined[8] giving results which may support this point of view, without excluding some sterical contribution.

These considerations agree also with the decomposition activation energies. They are markedly greater in the 3,5-PC compounds than in the 3,4-PC series, if different reaction orders are taken into account.

This behaviour also accounts for a greater reticular contribution when the 3,5-PC series is considered with respect to the other.

Unfortunately, when considering metal ion series, the activation energies do not follow a simple sequence and the determined reaction orders are not the same when considering decomposition reactions. In particular both compounds of cupric ion with 3,5-PC and 3,4-PC show a maximum in the activation energy with respect to the other metals, despite the minimum in the thermal stability estimated from the temperature range of decomposition. This fact may be attributed to different reaction mechanisms, mainly depending on the metal ion.

ACKNOWLEDGEMENT

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