

Thermal Decomposition Studies: Part VII*—Kinetics of Depyridination of Pyridine-thiocyanato Complexes of Mn(II), Ni(II), Cu(II) & Zn(II)

C. G. R. NAIR & P. INDRASENAN

Department of Chemistry, University of Kerala, Trivandrum 695001

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The thermal decomposition behaviour of $\text{Mn(Py)}_4(\text{SCN})_2$, $\text{Ni(Py)}_4(\text{SCN})_2$, $\text{Cu(Py)}_2(\text{SCN})_2$ and $\text{Zn(Py)}_2(\text{SCN})_2$ (Py = pyridine) is investigated by thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) techniques as well as by X-ray powder diffractometry. The Mn and Ni complexes show 2 depyridination peaks (corresponding to the loss of 2 pyridine molecules at each stage) followed by oxidative decomposition peaks. The Cu and Zn complexes show only 1 depyridination peak (where both the pyridine molecules are lost) followed by oxidative decomposition peaks. The depyridinated thiocyanates have narrow thermal stability plateaus; the ultimate decomposition products are the oxides, Mn_3O_4 , NiO, CuO (mixed with some CuSO_4) and ZnO, as shown by chemical analysis and X-ray powder patterns. The kinetic parameters (energy and entropy of activation) for the thermal depyridination stages have been evaluated by the Coats-Redfern Method.

THE formation of di- or tetrapyridino-dithiocyanato complexes by dipositive ions of some 3d-transition metals has been employed as the basis for the well known and rapid (time < 1 hr) gravimetric methods for the determination of these cations¹. However, apart from the early studies of Duval and coworkers², no detailed studies on the thermal decomposition of these complexes seem to have been carried out. Also no attempts have been made so far to study the kinetics of the thermal decomposition of these complexes. As part of our investigation on thermal decomposition kinetics of transition metal complexes³⁻⁸, we have now studied in detail the thermal decomposition, by simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) techniques, of four typical pyridine-thiocyanato complexes, viz. those of Mn(II), Ni(II), Cu(II) and Zn(II). Kinetic parameters, like energy and entropy of activation and pre-exponential factor have been calculated for the depyridination steps by a mathematical analysis of the TG curves and the results are reported in the present paper.

Materials and Methods

Preparation of the complexes—Pyridine-thiocyanato complexes of Mn, Ni, Cu and Zn were prepared by standard methods involving the addition of pyridine to a mixture of aqueous solutions of thiocyanate and the respective metal sulphates¹. The purity of the complexes were checked by elemental analyses (Table 1).

Apparatus—TG and DTA curves were simultaneously recorded on a Stanton recording thermobalance (model TRO1). The experimental conditions employed were: heating rate = 4° min⁻¹; chart speed = 3 inches hr⁻¹; atmosphere = static air; and

reference substance (DTA), $\alpha\text{-Al}_2\text{O}_3$. The samples (~35 mg, finely powdered) were taken in cylindrical deep platinum crucibles.

The X-ray powder patterns were taken on a Philips Debye-Scherrer camera with a diameter $5.73 \times 10^{-2}m$, employing Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$).

Independent pyrolysis experiments—The ultimate decomposition products in air were examined in every case by independent pyrolysis experiments, in which the samples were heated for 2 hr in silica crucibles to ~900°.

The intermediate depyridinated products were also examined by heating the complexes in air to appropriate temperatures in silica crucibles. The elemental analyses of these depyridinated products are also included in Table 1.

Treatment of data—The instrumental TG curves were redrawn as the mass vs temperature (TG) curves and also as the rate of loss of mass vs temperature (DTG) curves, using standard curve sets. The instrumental DTA curves were used as such. The plateaus in TG curves and the peak temperatures and the peak widths in DTG and DTA curves were noted.

Mathematical Analysis of TG Curves

The TG curves were studied in greater detail. The kinetic parameters, viz. order of the reaction (n), activation energy (E^*), the pre-exponential factor (Z), and the entropy of activation (ΔS^*) were calculated from the TG curves by a mathematical analysis as outlined below.

Determination of the order of reaction—The 'order of reaction' parameter n was obtained using the relation (1) suggested by Horowitz and Metzger,

$$C_s = n^{11-n} \quad \dots(1)$$

where C_s is the weight fraction of the substance present at the temperature T_s (the DTG peak tempe-

*For Part VI, see reference 8.

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES AND THEIR DECOMPOSITION PRODUCTS

Compound	Metal (%)		N (%)		S (%)	
	Found	Reqd	Found	Reqd	Found	Reqd
COMPLEXES						
Mn(Py) ₄ (SCN) ₂	11.31	11.28	17.11	17.26	12.96	13.14
Ni(Py) ₄ (SCN) ₂	11.89	11.96	17.07	17.12	12.90	13.04
Cu(Py) ₂ (SCN) ₂	18.91	18.83	16.66	16.60	18.84	18.97
Zn(Py) ₂ (SCN) ₂	19.21	19.26	16.43	16.50	18.74	18.86
EXPECTED DEPYRIDINATED PRODUCTS						
Mn(SCN) ₂	32.10	32.16	16.60	16.39	37.31	37.46
Ni(SCN) ₂	33.53	33.61	16.12	16.03	36.57	36.64
Cu(SCN) ₂	35.38	35.40	15.48	15.60	35.54	35.66
Zn(SCN) ₂	35.96	36.04	15.32	15.44	35.17	35.29

ature). A "master curve" between C_s and n was constructed as described earlier⁴ and from the experimentally determined value of C_s , n was read off from this curve. For all the depyridination steps, the order was found to be unity.

Evaluation of kinetic parameters — After determining n , an integral method was employed to evaluate kinetic parameters, in conformity with current trends in thermal analysis practice. For this purpose, the Coats-Redfern relation (2) was employed in the following form (suitable when $n = 1$, as in the present case):

$$\log \frac{\ln C^{-1}}{T^2} - \log \frac{ZR}{\phi E^*} - \frac{E^*}{2.303 RT} \quad \dots(2)$$

Here, $C = w_\infty - w/w_\infty$; w_∞ = total mass loss for the particular stage; w = mass loss at temperature T (°K), Z = pre-exponential factor; R = gas constant; ϕ = heating rate in degrees sec⁻¹. Plotting the LHS of Eq. (2) against $1/T$, linear plots were obtained. The slope of these gives $-E^*/2.303R$ from which E^* was calculated. The intercept gives $\log ZR/\phi E^*$ from which, knowing E^* , Z was calculated. The entropy of activation ΔS^* was calculated from the relation

$$Z = \frac{kT_s}{h} e^{\Delta S^*/R} \quad \dots(3)$$

where k is the Boltzmann constant, h is the Planck constant and T_s is the DTG peak temperature (°K).

All the linear plots were drawn by the method of least squares. The correlation coefficients (r) for the least square plots were also calculated.

Results and Discussion

Analytical data of the complexes and the depyridinated products are given in Table 1. Table 2 records the plateaus in TG and the peak temperatures and peak widths in DTG and DTA. Table 3 presents the kinetic parameters and also the correlation coefficients of the linear plots, while Table 4 gives the pyrolysis data. X-ray diffraction data of the decomposition products are reported in Table 5. All the temperatures are given in °C, unless otherwise specified.

TABLE 2 — PLATEAUS IN TG AND PEAK TEMPERATURES AND PEAK WIDTHS IN DTG AND DTA CURVES

Plateaus in TG curve (°C)	Peak temp. in DTG curve (°C)	Peak widths in DTG curve (°C)	Peak temp. in DTA curve (°C)	Peak widths in DTA curve (°C)
Mn(Py) ₄ (SCN) ₂				
Up to 100	161 s	120-190	163 m endo	130-170
260-300	237 s	190-270	241 m endo	190-250
420-700	332 m	290-370	338 s exo	290-370
875 onwards	392 w	370-430	389 m exo	370-450
	753 w	690-790	755 m endo	560-800
			830 m exo	800-840
Ni(Py) ₄ (SCN) ₂				
Up to 110	179 s	110-200	180 m endo	150-185
290-330	244 s	200-300	246 m endo	210-260
410-610	372 m	320-400	375 s exo	320-400
770 onwards			477 m exo	400-500
			680 m endo	500-690
			707 m endo	690-800
Cu(Py) ₂ (SCN) ₂				
Up to 140	193 s	130-230	193 m endo	150-195
240-260	309 w	230-330	310 m exo	230-330
410-600	359 w	330-370	345 s exo	330-350
810 onwards	675 w	630-710	372 s exo	350-430
			673 s endo	520-680
			702 m endo	680-750
Zn(Py) ₂ (SCN) ₂				
Up to 150	253 s	130-320	203 m endo	150-250
570-690	364 s	320-420	265 m endo	250-290
870 onwards	440 sh	420-520	368 s exo	310-410
	763 m	680-820	450 m exo	410-510
			526 m exo	510-550
			570 m exo	550-580
			768 s endo	580-790
			843 m exo	790-847
			852 m endo	847-870

s = strong; m = medium; w = weak; sh = shoulder; endo = endothermic; and exo = exothermic.

TABLE 3 — KINETIC PARAMETERS FOR THE DEPYRIDINATION OF PYRIDINE-THIOCYANATO COMPLEXES

 ["Order parameter" (n) = 1 for all the cases]

Compound	Stage	E^* kJ mole ⁻¹	Z cm ³ ($n-1$) mole ¹⁻ⁿ sec ⁻¹	ΔS^* J° K ⁻¹ mole ⁻¹	Correlation coefficient r
Mn(Py) ₄ (SCN) ₂	1	113.3	1.444×10^{11}	-34.42	0.9783
	2	160.8	1.362×10^{14}	21.20	0.9977
Ni(Py) ₄ (SCN) ₂	1	129.1	4.470×10^{12}	-6.194	0.9984
	2	146.0	1.777×10^{12}	-1.498	0.9723
Cu(Py) ₂ (SCN) ₂	1	186.8	3.430×10^{18}	106.2	0.9865
Zn(Py) ₂ (SCN) ₂	1	47.04	5.582×10^1	-216.1	0.9913

TABLE 4 — PYROLYSIS DATA

Compound	Probable pyrolytic residue after			Loss of mass (%) after						
	Stage 1	Stage 2	Final	Stage 1		Stage 2		Final		
				From TG data	Calc.	From TG data	Calc.	From TG data	From independ- ent pyrolysis	Calc.
Mn(Py) ₄ (SCN) ₂	Mn(Py) ₂ (SCN) ₂	Mn(SCN) ₂	Mn ₂ O ₄	33.96	32.45	63.13	64.90	75.39	76.23	77.49
Ni(Py) ₄ (SCN) ₂	Ni(Py) ₂ (SCN) ₂	Ni(SCN) ₂	NiO	34.62	32.20	63.58	64.40	83.49	84.30	84.78
Cu(Py) ₂ (SCN) ₂	Cu(SCN) ₂	—	CuSO ₄ + CuO	45.36	46.81	—	—	75.78	75.82	—
Zn(Py) ₂ (SCN) ₂	Zn(SCN) ₂	—	ZnO	42.73	46.55	—	—	75.56	75.84	76.02

TABLE 5 — X-RAY DIFFRACTION DATA

Parent complex	Pyrolytic residue (temp. in parentheses)	d spacings (Å) calc. from the obs. values	Intensity order observed	ASTM data file	
				d spacings (Å)	Intensity order
Mn(Py) ₄ (SCN) ₂	Mn(SCN) ₂ (260°) Mn ₂ O ₄ (900°)	No clear lines were obtained	1	2.77	1 (90)
			2	1.54	2 (80)
			3	1.58	3 (50)
Ni(Py) ₄ (SCN) ₂	Ni(SCN) ₂ (290°) NiO (900°)	2.82 2.28 2.09 2.41 1.50	1	2.83	1 (100)
			2	2.26	2 (33)
			1	2.09	1 (100)
			2	2.41	2 (91)
			3	1.48	3 (57)
Cu(Py) ₂ (SCN) ₂	Cu(SCN) ₂ (240°) CuSO ₄ CuO (900°)	5.54 1.90 2.66 2.43 2.52 2.34 1.88	1	5.50	1 (100)
			2	1.92	2 (50)
			1	2.62	1 (95)
			2	2.42	2 (50)
			1	2.52	1 (100)
			2	2.32	2 (96)
			3	1.87	3 (25)
Zn(Py) ₂ (SCN) ₂	Zn(SCN) ₂ (330°) ZnO (900°)	3.30 5.41 4.33 2.51 2.81 1.65	1	3.38	1 (100)
			2	5.40	2 (80)
			3	4.33	3 (48)
			1	2.48	1 (100)
			2	2.82	2 (76)
			3	1.63	3 (40)

Thermal behaviour — While it is true that the actual peak temperatures do not have much significance in view of their dependence on the sample mass, surface area and heating rate^{9,10}, it is nevertheless useful to make a comparison of the DTG and DTA peaks obtained under identical conditions, using simultaneous TG-DTA.

The Mn complex shows a stability plateau in TG up to ~100°. The elimination of pyridine takes place in two stages as shown by the two DTG peaks

at 161° and 237° which correspond with the two endothermic DTA peaks at 163° and 241° respectively. The first stage corresponds to the elimination of two pyridine molecules and the second stage represents the elimination of the remaining two pyridine molecules. The percentage loss of weight at the end of the first stage is 33.90% (theoretical value for the loss of two pyridine molecules = 32.45%) and that at the end of the second stage is 63.13% (theoretical value for the loss of all

the four pyridine molecules = 64.90%). The resulting compound is identified as $\text{Mn}(\text{SCN})_2$ by elemental analysis (vide Table 1). It is stable in the range 260° to 300° and it begins to decompose at ~300°. The DTG peak at 332° and the corresponding exothermic DTA peak at 338° represent this decomposition. The TG curve takes the horizontal at ~875° and final residue after ~900° is found to be Mn_2O_4 as supported by analysis and X-ray powder pattern data.

The Ni complex is stable up to ~110° and loses pyridine in two stages in a manner similar to that observed for Mn complex. The DTG peaks at 179° and 244° and the corresponding endothermic DTA peaks at 180° and 246° pertain to these stages. The weight losses at the two stages are in good agreement with the theoretical values (vide Table 4). The depyridinated compound is identified as $\text{Ni}(\text{SCN})_2$ by elemental analysis and by X-ray analysis. It is stable from 290° to 330° and begins to decompose at ~330°. The DTG peak at 372° and its closely corresponding exothermic DTA peak at 375° represent this stage. The TG curve becomes horizontal from ~770 and the final residue at ~900° is found to be NiO, as supported by elemental analysis and X-ray powder pattern data.

The Cu complex is stable up to ~140° and begins to lose pyridine after this temperature. The DTG peak at 193° and the corresponding endothermic DTA peak at 193° represent the single-stage elimination of pyridine molecules. The product at this stage conforms to the composition $\text{Cu}(\text{SCN})_2$. X-ray analysis confirms this. This product is stable from 240° to 260°. The DTG peak at 309° and the corresponding exothermic DTA peak at 310° represent the decomposition of the cupric thiocyanate. The final residue at ~900° is found to be a mixture of CuSO_4 and CuO, from analysis as well as from X-ray pattern.

The Zn pyridine thiocyanate is stable up to ~150° and the pyridine molecules are eliminated above 150°. The DTG peak at 253° and the corresponding endothermic DTA peak at 265° represent this stage. The product at this stage is identified as $\text{Zn}(\text{SCN})_2$ by elemental analysis and by X-ray powder pattern. The decomposition of the zinc thiocyanate begins as soon as the pyridine molecules are lost. This stage is denoted by the DTG peak at 364° and the corresponding exothermic DTG peak at 368°. The TG curve is horizontal after 870° and the final residue at ~900° is found to be pure ZnO from analysis as well as by X-ray examination.

Kinetics of depyridination—The kinetic parameters have been calculated for all the depyridination stages, viz. two stages each for the Mn and Ni complexes and one stage each for the Cu and Zn

complexes. It may be seen from the Table 3 that the order of the decomposition stages corresponding to the escape of pyridine is unity.

The energies of activation for the elimination of pyridine for all complexes except the Zn complex are in the range 100-200 kJ mole^{-1} . For the Zn complex it is only ~50 kJ mole^{-1} . These values are comparable to the usual values of the activation energies for dehydration of salt hydrates¹¹. The pyridine molecules in these complexes appear, therefore, to be bonded in an analogous fashion as the water molecules in salt hydrates. The process of depyridination of these complexes may thus be likened to the dehydration of salt hydrates and both processes take place at comparable temperature ranges too.

The lower value of E^* in the case of the Zn complex is rather difficult to explain; one may attribute it tentatively to the stereochemical consequences brought about by the completely filled $3d$ orbitals of Zn which gives it a status different from those of other $3d$ -transition metals. Thus, whereas the Zn complex is tetrahedral, the other three complexes are octahedral (or distorted octahedral or square planar); this would cause wide differences in the ligand field stabilization energy values.

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