

## **THERMAL STUDIES OF SOME MIXED COMPLEXES OF Mn(II) WITH PICRATE AND NITROGEN DONORS**

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The thermal decompositions of nine mixed ligand complexes of Mn(II) containing picrate and mono- or bidentate nitrogen ligands were studied by thermogravimetry. The kinetics of decomposition were examined by using the Coats-Redfern and Horowitz-Metzger equations; the decomposition was in all cases of the first order. The activation energies and other kinetic parameters were computed. The decomposition mechanisms exhibited a similar character for all the studied compounds. It was observed from the TG curves that the complexes decomposed to give six-coordinate intermediates, formed from substitution of the picrate into the inner coordination sphere. These intermediates decomposed to Mn(II) picrate and finally to Mn<sub>2</sub>O<sub>3</sub>.

### **Introduction**

Mn(II) picrate forms mixed ligand complexes with monodentate and bidentate nitrogen donor ligands [1-3]. The presence of different coordinating ligands in these complexes makes study of the thermal decomposition of these complexes of some interest, due to the possibility of a stepwise evolution of the involved ligands, and hence the formation of intermediates with possible stereochemical variations caused by heating. Therefore, and as an extension of our studies [4-6] on the thermal decomposition of mixed ligand complexes, we embarked on an investigation of the thermal decomposition of some mixed complexes of Mn(II) with picrate and nitrogen-containing ligands.

## Experimental

All chemicals used for the preparation of the complexes were of analytical grade. The complexes were prepared according to literature procedures [2, 3].

The thermogravimetric analyses were performed with a Sartorius 200 MP electrobalance converted to a thermobalance by the addition of a small furnace and sample holder. The temperature was measured with a Chromal-Alumal thermocouple attached to a Soar ME-550 digital multimeter; the heating rate was adjusted to be 7 deg/min.

## Results and discussion

The thermal decompositions of the complexes were examined in the temperature range 50–500°. From mass loss considerations, it was concluded that the end-product is  $Mn_2O_3$ . Two different methods involving the equations of Coats-Redfern [7] and Horowitz-Metzger [8], were used to evaluate the kinetic data from the TG curves.

### Coats-Redfern equation

The equation is used in the form

$$\log \log F(\alpha)/T^2 = \log ZR/\beta E(1-2 RT/E^*)-E^*/2.303 RT$$

where  $Z$ ,  $R$ ,  $\beta$  and  $E^*$  are the pre-exponential factor, gas constant, rate of heating and activation energy, respectively. The function  $F(\alpha) = -\log(1-\alpha)$  and the plot of  $-\log[-\log(1-\alpha)/T^2]$  vs.  $\frac{1}{T}$  result in a straight line of slope  $-E^*/2.303 R$ . The expression  $\log ZR/\beta E^*(1-2 RT/E^*)$  is constant for the temperature range over which reactions generally occur. Thus, the  $E^*$  values are calculated from the slopes of the straight lines. The activation enthalpy  $\Delta H^*$  is calculated from  $\Delta H^* = E-RT$ , while the activation entropy  $\Delta S^*$  is obtained from  $\Delta S^* = R[\ln(Zh/kT)-1]$ , where  $k$  is the Boltzmann constant, and  $h$  is the blank constant, assuming the transmission coefficient to be 1.

### Horowitz-Metzger equation

$$\log \left( \frac{W_o - W_f}{W - W_f} \right) = \frac{E^* \Theta}{2.303 RT_s^2} - \log 2.303$$

where  $W_o$  and  $W_f$  are the initial and final masses, respectively, and  $W$  is the mass at temperature  $T$ ;  $\Theta = T - T_s$ ,  $T_s$  is the temperature at the DTG peak;  $R$  is the gas constant and  $E^*$  is the energy of activation. The plot of  $\log \log \left( \frac{W_o - W_f}{W - W_f} \right)$  vs.  $\Theta$  gives a straight line, from the slope of which the activation energy  $E^*$  of decomposition can be determined.

It was found that the decompositions of all the complexes obey the equations of first-order decomposition reactions. The decomposition temperature ranges are given in Table 1.

The thermal behaviour of the complexes can be summarized as follows:

The stepwise course of the thermogravimetric curve (TG) of  $[\text{Mn}(\text{bpy})(\text{H}_2\text{O})_2](\text{pic})_2$  is characterized by three decomposition steps (Fig. 1). The first step is consistent with the elimination of  $2 \text{H}_2\text{O} + \text{bpy}$ , while the second one corresponds to the loss of the second bpy. The decomposition of the two picrate moieties takes place in the third step. The following equations illustrate the three decomposition steps:

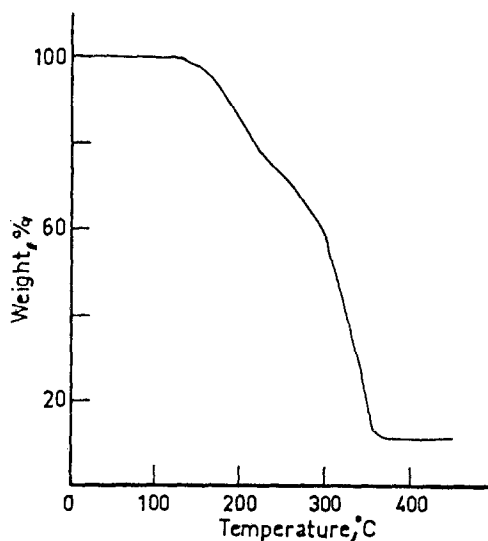
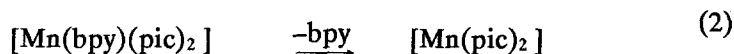
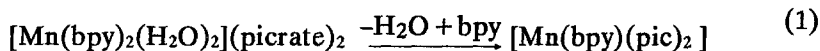
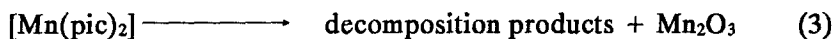


Fig. 1 TG curve of  $[\text{Mn}(\text{bpy})_2 \cdot \text{H}_2\text{O}]_2(\text{pic})_2$

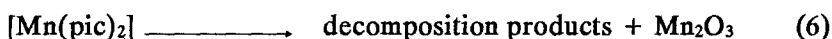
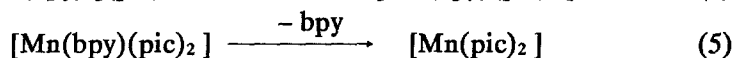
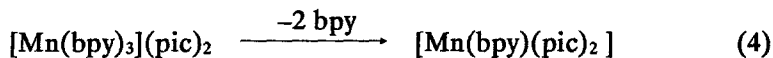
Table 1 Temperatures of decomposition and activation energies

Compound	T/ °C (DTG)			E* / kJ mol <sup>-1</sup> (Coats-Redfern)			E* / kJ mol <sup>-1</sup> (Horowitz-Metzger)		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
[Mn(bpy) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	203	250	325	45.95	13.74	58.09	52.51	23.80	54.77
[Mn(bpy) <sub>3</sub> ](pic) <sub>2</sub>	200	295	320	52.21	40.68	86.77	-	-	-
[Mn(phen) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	205	325	-	38.29	36.16	-	37.49	39.12	-
[Mn(phen) <sub>3</sub> ](pic) <sub>2</sub>	200	320	-	47.86	82.47	-	62.30	86.56	-
[Mn(py) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	150 180	215	300	59.00	31.91	44.59	65.48	40.53	54.12
[Mn(2-ampy) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	160	207	300	76.36	34.08	23.18	78.32	-	27.94
[Mn(qui) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	185	235	305	42.42	31.81	33.50	55.39	40.26	42.64
[Mn(en) <sub>3</sub> ](pic) <sub>2</sub>	160	195	240	82.97	24.77	-	82.84	20.77	-
[Mn(o-pda) <sub>3</sub> ](pic) <sub>2</sub>	170	270	320	42.54	19.14	-	51.24	26.34	-

pic = Picrate; bpy = Bipyridyl; phen = o-Phenanthroline; py = Pyridine; 2-ampy = 2-Aminopyridine; qui = Quinoline; en = Ethylenediamine; o-pda = o-Phenylenediamine



The complex  $[\text{Mn}(\text{bpy})_3](\text{pic})_2$  (Fig. 2) also undergoes stepwise decomposition in three distinct stages of weight loss. The first stage is commensurate with the evolution of two bpy molecules; the second stage correlates with the loss of the third bpy. The picrates are assumed to decompose in the third step:



For the complex  $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})_2](\text{pic})_2$ , two separate successive steps are observed. The first step accounts for the evolution of  $2 \text{ H}_2\text{O} + \text{phen}$ ; this step is immediately followed by a rapid second decomposition step, presumably corresponding to the decomposition of the second phen molecule, together with the picrates.

The decomposition of  $[\text{Mn}(\text{phen})_3](\text{pic})_2$  proceeds first in two slow steps, related to the elimination of 2 phen molecules. Afterwards, a rapid decomposition sets in (third step), which correlates with the decomposition of the third phen, together with the picrate part. Phenanthroline molecules can

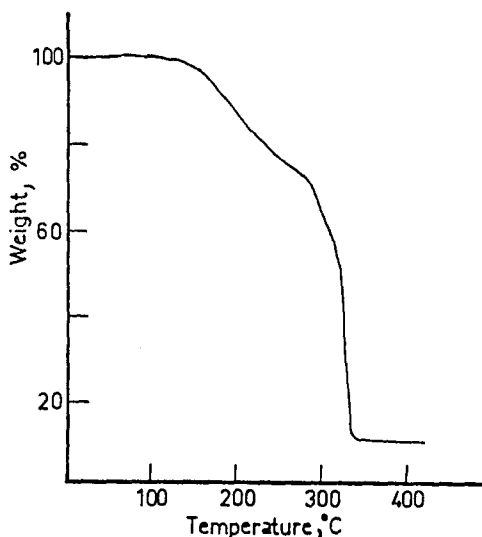
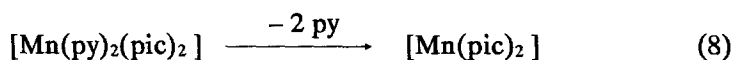
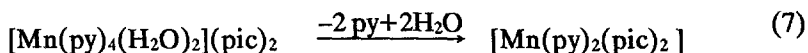


Fig. 2 TG curve of  $[\text{Mn}(\text{bpy})_3](\text{pic})_2$

break up while still coordinated to a metal ion [9] or can be converted to involatile polymeric products which are then oxidized to gaseous products [10]. These processes are also possible during the thermal decomposition of the above two phen complexes.

The TG curve of  $[\text{Mn}(\text{py})_4(\text{H}_2\text{O})_2](\text{pic})_2$  consists of four overlapping stages. The first and second steps can be identified from weight loss considerations as corresponding to the elimination of  $2 \text{H}_2\text{O} + 2 \text{py}$ ; the third step is consistent with volatilization of the remaining  $2 \text{py}$  molecules. The fourth stage is related to the decomposition of picrates:



The thermal curve of  $[\text{Mn}(2\text{-ampy})_4(\text{H}_2\text{O})_2](\text{pic})_2$  indicates a three-stage thermal decomposition. The first and second stages are consistent with the elimination of  $2 \text{H}_2\text{O} + 2 \text{2-ampy}$  and  $2 \text{2-ampy}$ , respectively. The third step relates to the decomposition of the two picrate moieties.

The complex  $[\text{Mn}(\text{quin})_4(\text{H}_2\text{O})_2](\text{pic})_2$  yields a TG thermolysis curve consisting of three decomposition steps corresponding to the elimination of  $2 \text{H}_2\text{O} + 2 \text{quin}$  and  $2 \text{quin}$ , and the decomposition of picrate, respectively.

The TG curve of  $[\text{Mn}(\text{en})_3](\text{pic})_2$  exhibits three decomposition steps. The mass changes associated with the first and second steps are correlated with the evolution of  $2 \text{en}$  molecules and one  $\text{en}$  molecule, respectively. The third step represents a rapid loss in weight due to picrate decomposition.

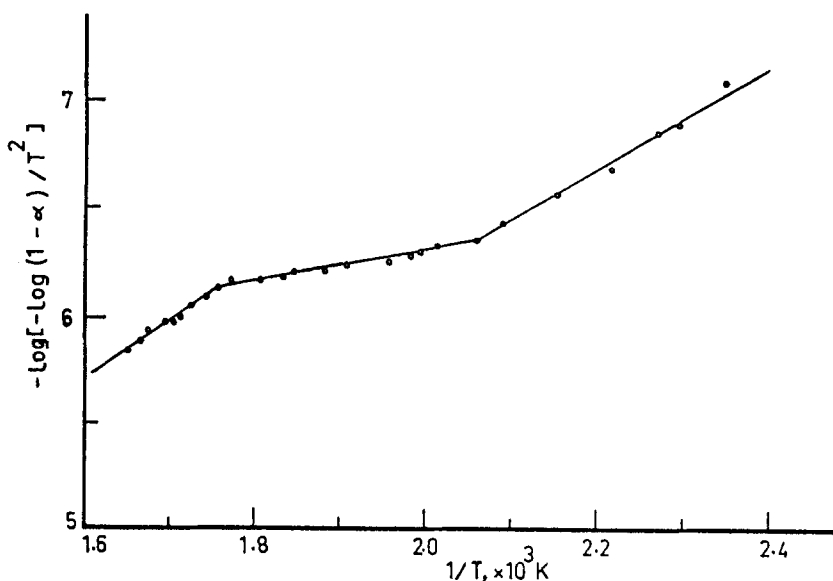
An examination of the TG curve of  $[\text{Mn}(\text{o-pda})_3](\text{pic})_2$  indicates that the curve consists of three discontinuities. The first one involves the elimination of  $2 \text{o-pda}$  molecules, the second is correlated with the loss of one  $\text{o-pda}$  molecule, and the third is associated with the decomposition of the picrates.

The activation energies, activation enthalpies and activation entropies of the different decomposition steps for each complex are recorded in Tables 1 and 2.

There are no obvious trends in the activation energies or the activation enthalpies. However, the negative values of the activation entropies indicate that the activated complex has a more ordered structure than the reactants, and that the reactions are slower than normal [11]. Coats-Redfern and Horowitz-Metzger linearization curves are shown in Figs 3 and 4.

Table 2 Kinetic parameters of decomposition

Compound	$\Delta H^* / \text{kJ mol}^{-1}$			$\Delta S^* / \text{kJ mol}^{-1}$		
	stage			stage		
	(1)	(2)	(3)	(1)	(2)	(3)
[Mn(bpy) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	42.05	9.39	53.11	-71.25	-70.70	-62.06
[Mn(bpy) <sub>3</sub> ](pic) <sub>2</sub>	48.27	35.95	81.39	-85.30	-65.99	-66.33
[Mn(phen) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	34.31	31.18	—	-73.33	-63.86	—
[Mn(phen) <sub>3</sub> ](pic) <sub>2</sub>	43.92	78.03	—	-175.94	-65.46	—
[Mn(py) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	100.66 55.23	28.18	39.78	-68.48 -50.87	-65.27	-68.07
[Mn(2-ampy) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	72.76	30.08	18.41	-70.15	-75.09	-76.59
[Mn(quin) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](pic) <sub>2</sub>	38.61	27.58	28.69	-80.92	-63.65	-69.32
[Mn(en) <sub>3</sub> ](pic) <sub>2</sub>	79.37	20.87	—	-77.62	-83.04	—
[Mn(o-pda) <sub>3</sub> ](pic) <sub>2</sub>	47.55	21.82	—	-82.24	-72.13	—

Fig. 3 Coats-Redfern plots for the decomposition of [Mn(bpy)<sub>2</sub>·H<sub>2</sub>O)<sub>2</sub>](pic)<sub>2</sub>

In order to account for the stepwise decomposition of the complexes, we may first propose that the bases are not equivalent or bonded in different ways in the initial complexes, where this factor may play an important role if one molecule of the volatile component is in the coordination sphere, while another is in the crystal lattice, e.g in Cu(H<sub>2</sub>O)<sub>4</sub>SO<sub>4</sub>·H<sub>2</sub>O, where stepwise

decomposition may be expected. The published IR spectral data [2, 3] provide no evidence of such inequivalence of the coordinated amines.

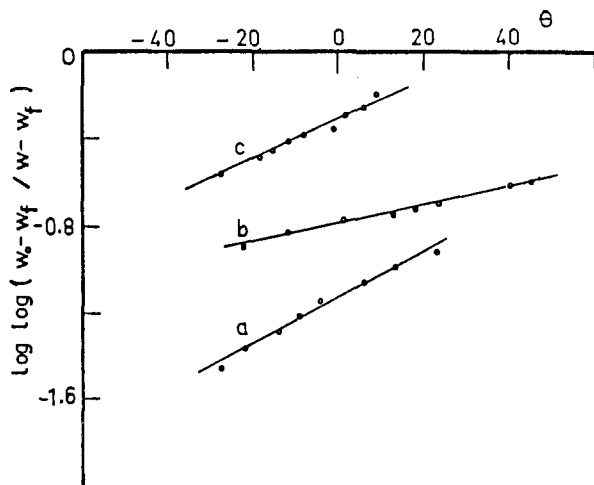


Fig. 4 Horowitz-Metzger plots for the three thermal decomposition steps of  $[\text{Mn}(\text{bpy})_2 \cdot \text{H}_2\text{O}]_2(\text{pic})_2$ . (a) first step (b) second step and (c) third step

It is most probable that the stepwise occurrence of the process depends on the stabilities of the octa- or tetracoordinate complexes produced upon release of the bases from the parent octahedral complexes. We proposed that the two ionic picrates in the parent complexes substitute the amines in the coordination sphere (Eqs 1, 4 and 7) so as to retain the octahedral structure around the Mn(II); coordination of only one picrate ion to Mn(II) to produce ionic tetracoordinate complexes is also a possibility. Unfortunately, it was difficult to isolate these intermediates, due to their rapid decomposition. Substitution of the counter ions for the coordinated ligands in the inner coordination sphere has been reported for the tris-(*o*-phen) complexes of some first transition elements upon their thermal decomposition [12].

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**Zusammenfassung** — Mittels Thermogravimetrie wurde die thermische Zersetzung von neun Mn(II)-Mischligandenkomplexen mit Pikrat und mono- oder dizahnligen Stickstoffliganden untersucht. Die Kinetik der Zersetzung wurde mittels der Coats-Redfern und der Horowitz-Metzger-Gleichungen untersucht; in jedem Falle handelt es sich um eine Kinetik erster Ordnung. Die Aktivierungsenergie und andere kinetische Parameter wurden berechnet. Der Mechanismus der Zersetzungsreaktion zeigt für alle untersuchten Verbindungen einen ähnlichen Charakter. Anhand der TG-Kurven wurde beobachtet, daß bei der Zersetzung der Komplexe durch Substitution des Pikrates in die inneren Koordinationssphäre Zwischenprodukte mit der Koordinationszahl sechs entstehen. Diese Intermediäre zersetzen sich über Mn(II)-pikrat zu  $Mn_2O_3$ .