

TG, DTA AND HPLC STUDIES OF THE THERMAL DECOMPOSITION OF THE BIS(4-CARBOXYMETHYL PYRIDINE) BIS(DIMETHYL GLYOXIMATO)IRON(II) COMPLEX

Henrique E. Toma, Alcione M. Ykeuti, Mauro C. Silva and Luiz A. Morino.

Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, SP.

Recebido em 08/03/89

**Abstract** - The thermal decomposition of the bis(4-carboxymethyl pyridine) bis(dimethyl glyoximato) iron(II) complex was investigated based on TG and DTA techniques. The endothermic loss of the 4-carboxymethyl pyridine ligands was observed at 145 °C and was followed by an exothermic reaction, yielding volatile products such as 2,3-butanedione and dimethyl furazan.

Introduction

We report here the thermal behaviour of a typical macrocyclic iron-dioxime complex. The subject is of current interest, since the thermal decomposition of iron-macrocyclic complexes has frequently been employed in the synthesis of new low dimensional materials.<sup>1</sup>

Experimental Section

The  $[\text{Fe}(\text{Hdmg})_2(\text{pcmpy})_2]$  complex (Hdmg = dimethyl glyoximato anion, pcmpy = 4-carboxymethyl pyridine) was synthesized by reacting iron(II) acetate (0.2 g, 0.011 mole) with the corresponding  $\text{H}_2\text{dmg}$  (2.75 g, 0.023 mole) and pcmpy (9 g, 0.075 mole) ligands, in methanol (100 ml), under an argon atmosphere. The procedures employed in the synthesis and characterization of the complex were similar to those previously reported in the literature.<sup>2,3</sup> Anal: Calcd for  $\text{C}_{22}\text{H}_{28}\text{O}_8\text{N}_6\text{Fe}$ : C, 47.2; H, 5.04; N, 15.0. Found: C, 47.3, H, 5.03; N, 14.9.

TG and DTA measurements were carried out using Shimadzu model TG 20 and DTA 203 equipments, at a heating rate of 5 deg/min, under a flow of nitrogen (100 ml/min). The pyrolysis was also carried out in a tubular oven, under a flow of nitrogen, using a heating rate of 20 deg/min. After passing through a glass wool filter, the flow of nitrogen carrying the volatile species was bubbled into a series of washers containing HPLC grade methanol. The products were analysed using a Merck Lichrocart RP-18 column, with a CG-480 HPLC instrument, equipped with a HP-8451-A

visible-uv diode-array detector.

Results and Discussion

TG and DTA curves for the  $[\text{Fe}(\text{Hdmg})_2(\text{pcmpy})_2]$  complex can be seen in Fig. 1. The decomposition reaction starts at 140 °C, with a rapid weight loss, coinciding with a sharp endothermic peak at 142 °C. After this point, a strong exothermic reaction takes place, exhibiting a peak temperature around 205 °C. Similar exothermic peaks have also been observed in the pyrolysis of cobalt(III)-dioxime complexes.<sup>4</sup>

HPLC analyses of the volatile products are shown in Figs. 2 and 3. The axial ligand was readily identified by its uv absorption spectrum, as the major species (peak E), corresponding to 2 moles of pcmpy for each mole of  $[\text{Fe}(\text{Hdmg})_2(\text{pcmpy})_2]$ . Formation of 2,3-butanedione (peak B) was evidenced by its characteristic smell, and by its absorption band at 206 nm, corresponding approximately to 0.4 mole for each mole of complex. The spectrum corresponding to peak D coincides with the absorption spectrum of dimethyl furazan ( $\lambda_{\text{max}} = 210 \text{ nm}$ , Sadtler Catalog 7673 UV). This heterocyclic molecule is usually obtained by the dehydration of dimethyl glyoxime.<sup>5</sup> In our case, the thermal decomposition of one mole of the complex

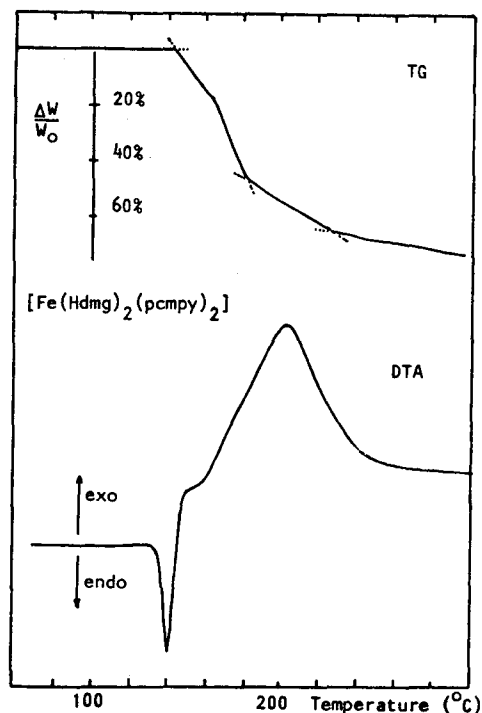


Fig. 1. TG and DTA curves for the  $[\text{Fe}(\text{Hdmg})_2(\text{pcmpy})_2]$  complex ( $\Delta W/W_0$  = relative weight loss).

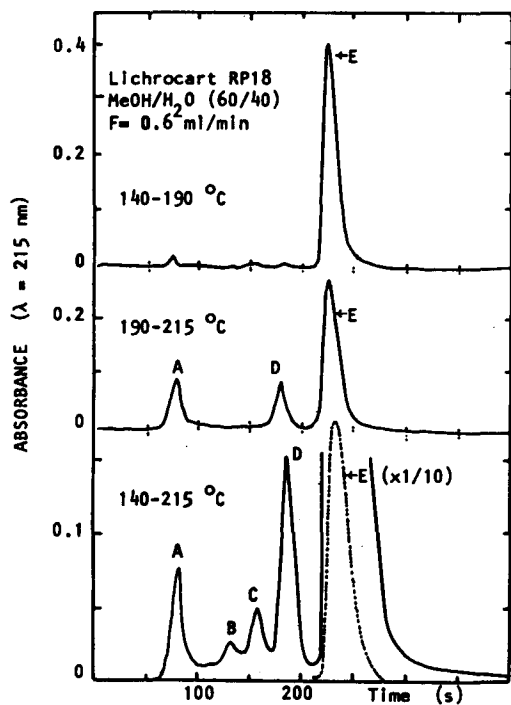


Fig. 2. Chromatograms of the volatile products resulting from the pyrolysis of the  $[\text{Fe}(\text{Hdmg})_2(\text{pcmpy})_2]$  complex, at several temperatures.

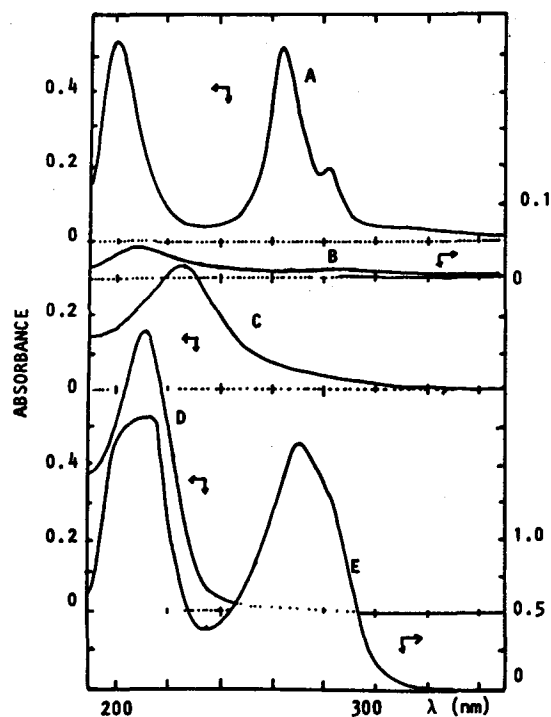
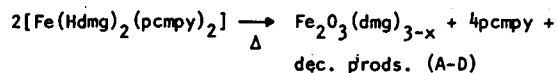


Fig. 3. Fast scanning spectra of the volatile products from the pyrolysis of the  $[\text{Fe}(\text{Hdmg})_2(\text{pcmpy})_2]$  complex, corresponding to peaks A-E in Fig. 2.

yielded 0.4 mole of dimethyl furazan. Dimethyl glyoxime is released in very small amounts, corresponding to peak C in Fig. 2. Peak A has also been observed in exploratory experiments with  $[\text{Fe}(\text{Hdmg})_2\text{L}_2]$  complexes where L = pyridine, pyrazine and N-methyl imidazole. Therefore, it depends on the nature of the axial ligands. The absorption spectrum (Fig. 3) is similar to those of aromatic N-heterocyclic compounds such as the substituted pyrazines. The species probably results from the condensation of unsaturated oxime and carbonyl products; however, the identification has been complicated by the small yields and by its slow decomposition in solution.

The loss of the axial ligands starts below 180 °C (Fig. 2), leading to  $[\text{Fe}(\text{Hdmg})_2]$  species exhibiting an incomplete coordination environment. At higher temperatures an exothermic reaction takes place, involving the reduction of the oxime ligands by the iron(II) ions. The solid residue collected after the pyrolysis at 250 °C was black, showing the approximate composition: C, 26; N, 14; and H, 3%. It was slightly soluble in water, but dissolved in the presence of hydrochloric acid, e. g. 0.10 M, yielding solutions containing iron(III) species. The composition of the solid, however, is temperature dependent.

A variable composition,  $\text{Fe}_2\text{O}_x(\text{dmg})_{3-x}$ , can be suggested, according to the equation,



where x increases with the temperature, approaching 3 at 400 °C.

**Acknowledgements.** The support from FAPESP and CNPq is gratefully acknowledged.

#### References

- Hanack, M.; Deger, S.; Lange, A.; *Coord. Chem. Rev.*, (1988) **83**, 115.
- Pang, I. W.; Stynes, D. V.; *Inorg. Chem.*, (1977) **16**, 590.
- Toma, H. E.; Morino, L. A.; Santos, P. S.; *Inorg. Chim. Acta*, (1985) **108**, L25.
- Varhelyi, C.; Zsako, J.; Liptay, G.; Finta, Z.; *J. Thermal Anal.* (1987) **32**, 785.
- Gilchrist, T. L.; "Heterocyclic Chemistry", Pitman Publ., London, (1985), p. 222.