Thermochimica Acta, 78 (1984) 135–140
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF DINITROGEN COMPLEXES OF Fe(II) WITH CHELATING AGENTS

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(Received 13 February 1984)

ABSTRACT

The thermal decomposition of two dinitrogen complexes of iron with EDTA and CDTA have been studied using DTA and TG techniques. Intermediate products in the decomposition processes were characterized by IR spectroscopy. For both compounds the loss of dinitrogen occurs at ca. 230 °C, and it is accompanied by the disappearance of the $\nu_{N\equiv N}$ band in the IR spectra of the intermediate products. Na_2O and FeO are obtained as final products at 900 °C.

INTRODUCTION

The stability of dinitrogen complexes is still a confused problem and much work must be done in the future to clarify it. It is a well-known fact that in complexes where donation of electrons via π-bonding to the ligand is extensive, any decrease in the metal electron density results in the loss of the π-bonded ligand. Therefore, most dinitrogen complexes are unstable with respect to oxidation and decompose in air [1].

In the thermal decomposition of dinitrogen complexes, the elimination of N_2 is normally observed at temperatures ranging from 20 to 200 °C [2,3]. This communication studies the thermal decomposition processes for two dinitrogen complexes of iron with EDTA (ethylenediaminetetracetic acid) and CDTA (1,2-diaminecyclohexanetetracetic acid), using DTA and TG techniques. Intermediate products were characterized by IR spectroscopy in the same way as previously applied to study the thermal decomposition of aminopolycarboxylic ligands [4–7] and some of their complexes [8–10].

EXPERIMENTAL

The syntheses of the compounds $Na_2|Fe(EDTA)N_2| \cdot 2\ H_2O$ and $Na_2|Fe(CDTA)N_2| \cdot 2\ H_2O$ have been reported previously [11]. DTA and

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TG curves were obtained using a Mettler TA-HE-20 system with Pt/Pt–10% Rh thermocouples; α-Al_2O_3 was used as reference material in the DTA measurements. The heating rate was 10 °C min^{-1} in all cases. The experiments were carried out in an atmosphere of static air. Infrared spectra of solid intermediate products were recorded in KBr pellets using a Pye-Unicam SP 3-300 spectrophotometer.

RESULTS AND DISCUSSION

To make a comparative study of the thermal behaviour of both dinitrogen complexes, their thermal analyses have been divided in four steps:

(1) loss of crystallization water;

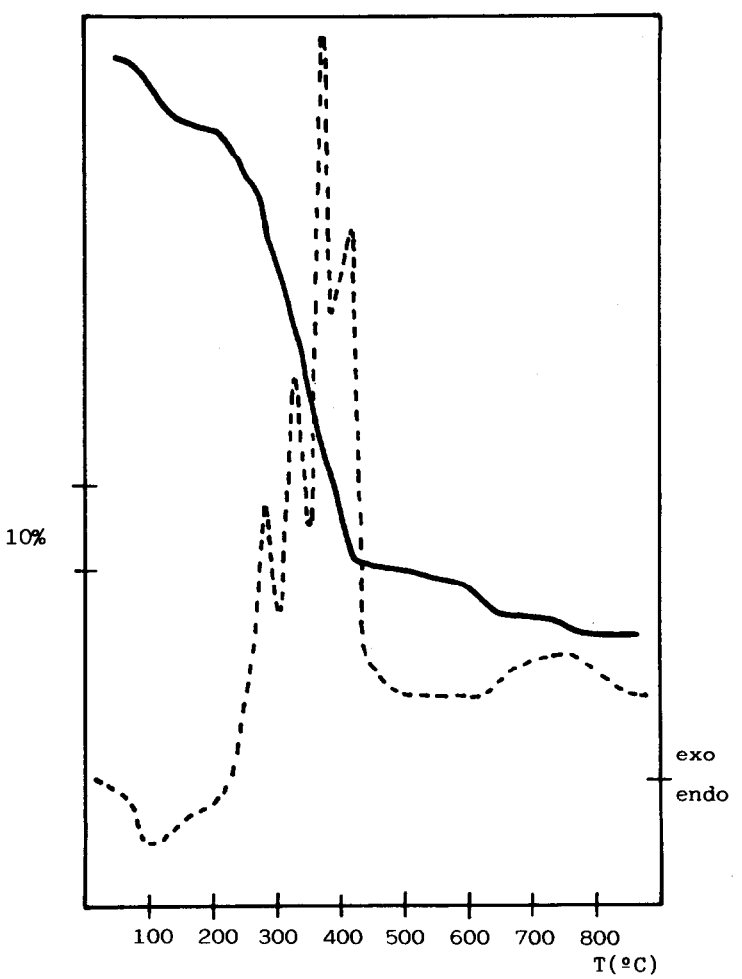

Fig. 1. DTA and TG curves for $Na_2|Fe(EDTA)N_2|\cdot 2\ H_2O$

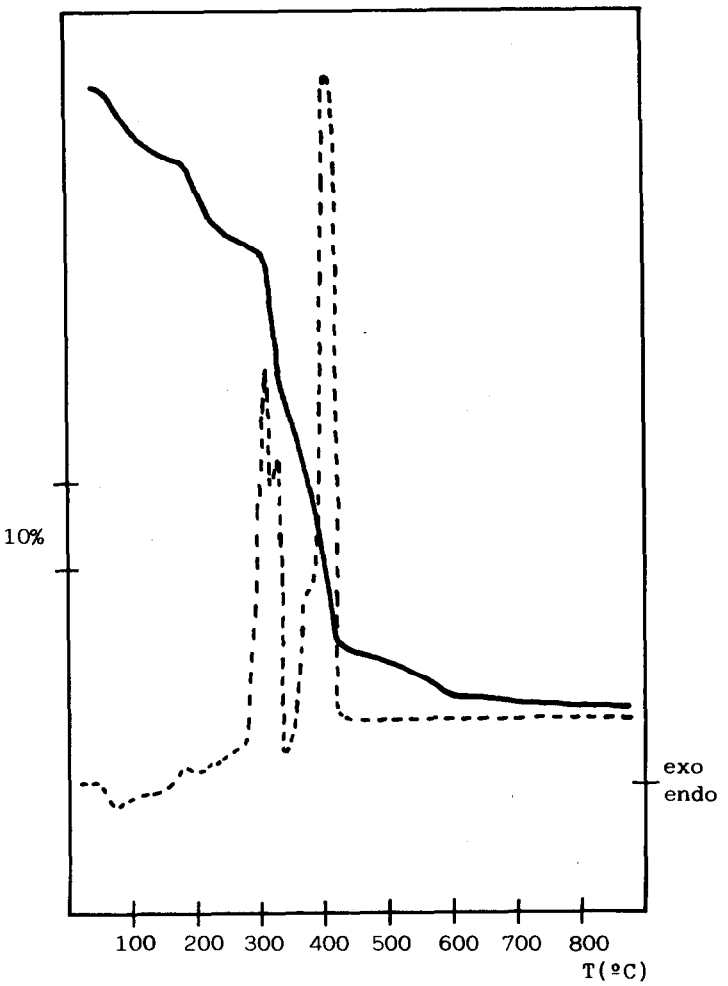

Fig. 2. DTA and TG curves for $Na_2|Fe(CDTA)N_2|\cdot 2\ H_2O$

(2) elimination of dinitrogen ligand;
(3) pyrolysis of the compound;
(4) formation of final products at 900 °C.

Figures 1 and 2 show the TG and DTA curves corresponding to the complexes of EDTA and CDTA, respectively. The IR spectra of some intermediate products corresponding to the thermal decomposition are shown in Figs. 3 (EDTA complex) and 4 (CDTA complex).

Loss of crystallization water

For both compounds there is a weight loss between 50 and 200 °C associated with endothermic effects in the DTA curves and corresponding to the elimination of two molecules of water. The theoretical values for the

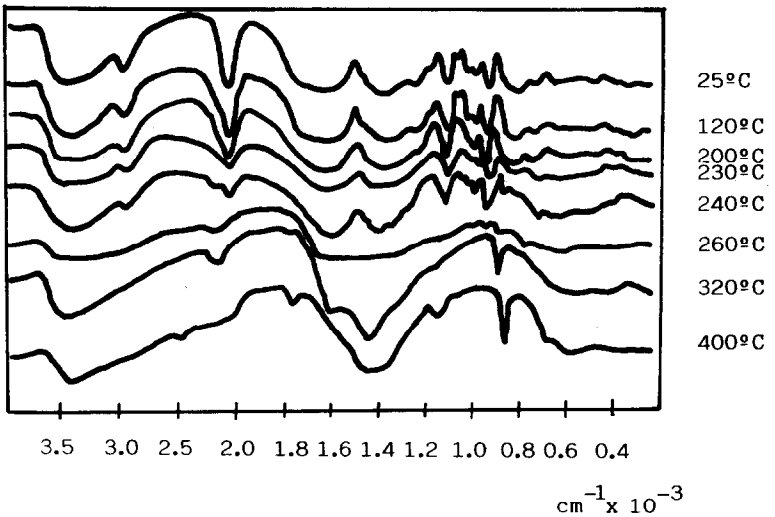

Fig. 3. IR spectra of some intermediate products in the decomposition of $Na_2[Fe(EDTA)N_2]\cdot 2H_2O$

complexes of EDTA and CDTA (7.93 and 7.09, respectively) are close to the experimental values (8.0 and 9.0%). Due to the hygroscopic nature of these samples it has not been possible to observe this process in the IR spectra of intermediate products at 200 °C.

Elimination of dinitrogen ligand

The IR spectra of intermediate products at temperatures higher than 200 °C (Figs. 3 and 4) show a loss of intensity of the $\nu_{N\equiv N}$ band until its disappearance. However, a new band appears centered at ca. 2200 cm^{-1}. This band is not considered to correspond to a new way of dinitrogen coordination because a similar band was observed in the thermal study of sodium salts of EDTA [6] and it was assigned to resonant double bonds between C and N. This overlap of dinitrogen elimination with the first stage of the pyrolysis of the compound causes the differences between the theoretical values of weight loss for the elimination of one molecule of N_2 (6.17 and 5.54% for the complexes of EDTA and CDTA, respectively) and the experimental values found between 200 and 300 °C in the TG curves (7% for both complexes).

The higher temperature of dinitrogen elimination for the CDTA complex (235 °C vs. 220 °C for the EDTA complex) seems to reflect a higher stability of $Fe-N_2$ bonds that is also observed in the lower frequency at which the $\nu_{N\equiv N}$ band appears in the CDTA complex.

Pyrolysis of the compound

Several exothermic effects appear in the DTA curves (Figs. 1 and 2) at temperatures higher than 300 °C. These effects are not observed when the

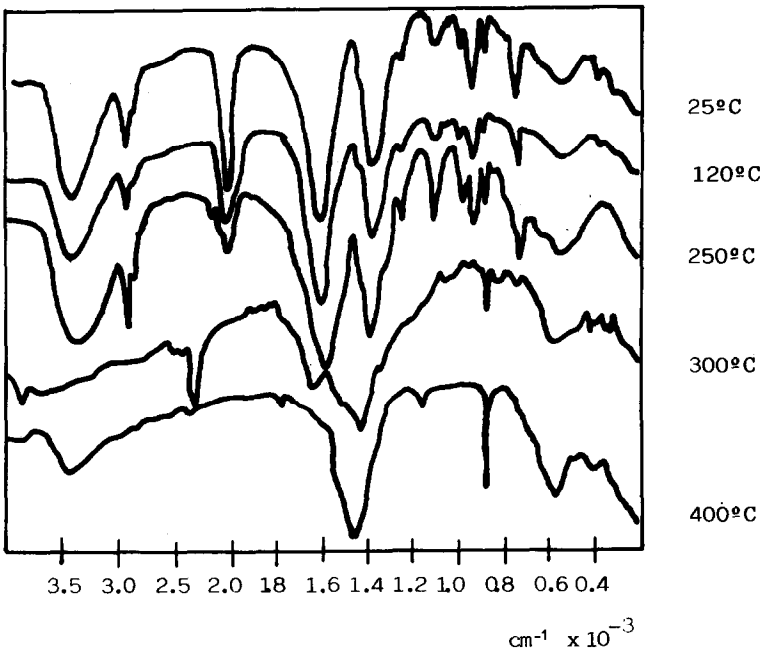

Fig. 4. IR spectra of some intermediate products in the decomposition of $Na_2[Fe(CDTA)N_2] \cdot 2\,H_2O$

experiments are carried out in an atmosphere of argon and correspond to the combustion of the organic material. The appearance of several peaks in the DTA curves suggests that this pyrolysis process occurs in different overlapping steps.

The disappearance of $\nu^{s}_{COO^-}$ (1400 cm^{-1}) and $\nu^{as}_{COO^-}$ (1600 cm^{-1}) bands in the IR spectra shows that this step of the decomposition process consists of the loss of the carboxylate groups associated with cracking and release of CO_2, CO, NH_3 and traces of hydrocarbons as shown in the thermal decomposition of sodium salts of EDTA and CDTA [6,7].

The IR spectra at 400 °C show a broad band at 1400 cm^{-1} and another one between 800 and 900 cm^{-1}. These bands are characteristic of carbonate ions, and because $FeCO_3$ decomposes at ca. 200 °C with FeO formation, the products formed after this stage must be Na_2CO_3 and FeO. The corresponding theoretical values of the weight loss from the anhydrous compounds (52.97 and 57.87% for the EDTA and CDTA complexes, respectively) agree well with the experimental values (52.3% for the EDTA complex and 56.5% for the CDTA complex).

Formation of final products at 900 °C

From the pyrolysis final temperature to 900 °C, an additional weight loss is still observed in the TG curves (Figs. 1 and 2) of both compounds with

values of 8.0 and 6.5% for the EDTA and CDTA complexes, respectively.

The study of the decomposition of sodium salts of EDTA and CDTA showed at these temperatures the decomposition of Na_2CO_3 with Na_2O formation [6,7], therefore, the same process must be observed for their iron complexes although the final products must be a mixture of Na_2O and FeO. In fact, the values of the total weight loss for the formation of these products are in agreement with the experimental values of 68.3 and 72.0% found for the EDTA (theor., 70.5%) and CDTA (theor., 73.6%) complexes, respectively.

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